

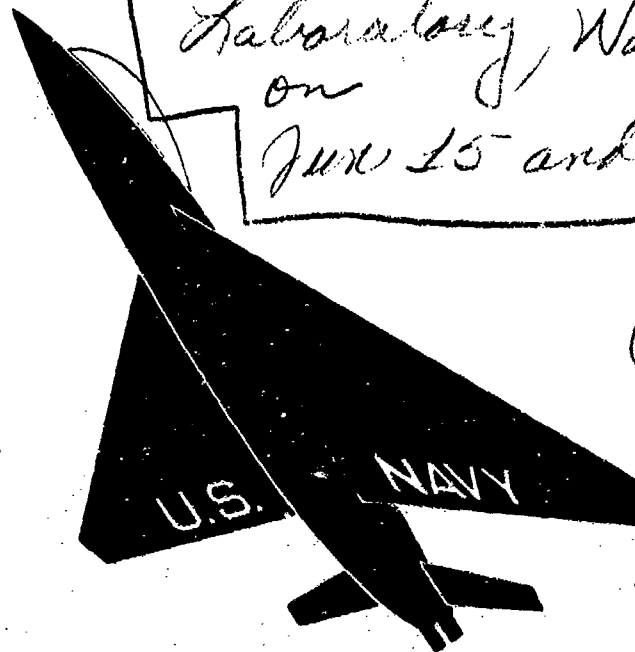
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**NAVAL AIR SYSTEMS COMMAND-
NAVAL RESEARCH LABORATORY WORKSHOP
ON BASIC RESEARCH NEEDS FOR
SYNTHETIC HYDROCARBON JET AIRCRAFT FUELS**

*held at Naval Research
Laboratory, Washington, D.C.
on
Jun 15 and 16 1978.*

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FOREWORD

"BASIC RESEARCH NEEDS FOR SYNTHETIC HYDROCARBON JET AIRCRAFT FUELS"

The Naval Air Systems Command and the Naval Research Laboratory jointly sponsored a Workshop on the topic "Basic Research Needs for Synthetic Hydrocarbon Jet Aircraft Fuels." The Workshop was held at the Naval Research Laboratory in Washington, D. C. on June 15 and 16, 1978.

The Workshop emphasized the technical aspects of synthetic jet fuels. The purpose was to examine what is known about synfuels, highlight current research programs, and suggest areas of basic research which are important to the future use of synthetic hydrocarbon fuels in jet aircraft.

Sponsor - Hyman Rosenwasser - Naval Air Systems Command

Organizing Committee:

Robert Hazlett - Naval Research Laboratory

Larry Maggitti - Naval Air Propulsion Center

Jeffrey Solash - Naval Research Laboratory

NAVAIR - NRL WORKSHOP

June 15, 1978

9:00 Session I - R. N. Hazlett presiding

- A. Welcome - CAPT Carleton Cooper - Naval Air Systems Command
- B. Keynote - John Pichtelberger - Naval Air Propulsion Center
"Availability and Performance of Jet Fuels"
- C. Shale Oil II - Update
 - 1. LCDR Larry Lukens - Naval Material Command
"Programs and Shale Crude Oil Production"
 - 2. Larry Kruse - Sohio
"Pilot Plant Refining Studies"
- D. Refining Studies
 - 1. William Dukek - EXXON R & E Co.
"Jet Fuels: The Refiner's Outlook"
 - 2. Richard Sullivan - Chevron Research Co.
"Refining Studies on Shale Oil"
- E. James Patton - Office of Naval Research
"ONR Programs in Combustion and Chemical Kinetics"
- F. Albert Antoine - National Aeronautics and Space
Administration
"Fuel Property Studies at NASA - Lewis"

1:15 Session II - Larry Maggitti presiding

- A. Fuel Stability
 - 1. C. J. Nowack - Naval Air Propulsion Center
"Thermal Oxidative Stability of Synthetic
Jet Fuels"
 - 2. John Frankenfeld - EXXON R & E Co.
"Storage Stability and Nitrogen Chemistry"
 - 3. Dennis Brinkman - Bartlesville Energy Technology Center
"Synfuel Storage and Thermal Stability Test Results"
 - 4. Robert Hazlett - Naval Research Laboratory
"CRC Literature Survey on Thermal Oxidative Stability
of Jet Fuels"

B. Combustion Properties

1. David Naegeli - Southwest Research Institute
"Combustion Experiments with Synthetic Jet Fuels"
2. Charles Martell - Wright-Patterson AFB
"AF Combustion Studies and Plans"

C. Low Temperature Properties

1. Wilbur Affens - Naval Research Laboratory
"Freezing Point Relationships of Jet Fuels"
2. C. T. Moynihan - Catholic University
"Composition and Temperature Dependence of Shear Viscosity of Hydrocarbon Mixtures"

June 16, 1978

9:45 Session III - Jeffrey Solash presiding

A. Jet Fuel Additives

1. Cy Henry - duPont Co.
"Behavior and Interactions"
2. Larry Maggitti - Naval Air Propulsion Center
"Smoke Suppressant Additives"

B. Jet Fuel Analysis

1. Harry Dorn - Virginia Polytechnic Institute
"Analysis of Jet Fuels by Nuclear Magnetic Resonance"
2. S. E. Buttrill - Stanford Research
"Analysis of Jet Fuels by Mass Spectrometry"

C. LCDR Leigh Doptis - U. S. Naval Medical R&D Command
"Comparative Toxicity of Petroleum and Oil Shale Derived Fuels"

D. Rex Neihof - Naval Research Laboratory
"Microbiological Studies of Jet Fuels"

E. Robert Hazlett - Naval Research Laboratory
"Basic Research Needs"

F. Homer Carhart - Naval Research Laboratory
Summary

WELCOME ADDRESS

CAPTAIN CARLETON COOPER

NAVAL AIR SYSTEMS COMMAND

As Assistant Commander for Research and Technology of the Naval Air Systems Command I am pleased to welcome you to this NAVAIR/NRL-sponsored workshop which emphasizes the research needed to provide synthetic jet fuels from alternative energy sources.

The incentive for this gathering is the knowledge that petroleum resources are part of nature's dwindling commodities. There are, of course, frantic efforts underway to postpone our eventual loss of this significant raw material by the search for new oil deposits. Among these efforts may be mentioned the use of the famous Glomar vessel for exploration of the deep oceans, a project sponsored by the National Science Foundation and the Geological Survey. Another project depends on huge loans from the World Bank to the so-called Third World nations for the same purpose.

Yet despite an occasional important discovery of oil deposits, as in the Alaskan and North Sea areas, a continual supply of petroleum-based fuels seems doomed, regardless of price. This gloomy situation, however, is somewhat brightened by our country's vast deposits of coal and oil shale for the eventual production of synthetic or alternate fuels. Much research and development are nevertheless still needed before these fossil sources are reborn to serve an evergrowing civilian and military need.

The Naval Air Systems Command is mindful of the efforts sponsored or carried out by the government agencies and other groups represented here today. For many years NAVAIR, too, has sponsored R&D fuel programs.

These dealt primarily with problems associated with JP-5 aircraft fuel and involved such aspects as thermal oxidative stability and fire safety. Our present concern with the synthetic fuel situation will be reported on by several of the speakers here present.

In closing I should like to commend Dr. Hazlett for putting together an all-encompassing program on hydrocarbon jet fuels and for providing the necessary expertise to discuss the subject under consideration. It is to be hoped that the sharing of data and ideas here will expedite our goal to provide the needed products from alternative energy sources.

KEYNOTE ADDRESS

JOHN PICHTELBERGER

NAVAL AIR PROPULSION CENTER
TRENTON, N. J.

AVAILABILITY OF PERFORMANCE OF JET FUELS

Fuel in the past has been a relatively constant factor in the development of aircraft. However, that situation may not continue very far into the future. We are rapidly approaching the situation where decisions must be made in regard to the characteristics of future JP-5. Some of the pressures on the aircraft/fuel relationship are shown in figure 1. The lower quality petroleum crudes contain a greater percentage of higher boiling materials which require additional processing to produce sufficient middle distillate fuels. The synthetic crudes which will become available during the late 1980's require additional processing to remove impurities such as nitrogen and to reduce the aromatic content for aircraft fuels. Fuel processing energy efficiency has to be considered since we are trying to conserve energy and the increased use of hydrogen along with severe hydrogenation pressure and temperature conditions is not conducive to energy conservation (or minimum cost). In regard to safety, a significant effort is underway to decrease fuel flammability through the use of antimisting additives. These additives, which are detrimental to the fluidity of fuels, will require changes to aircraft and engine fuel systems. Navy aircraft normally have a 20-30 year life span so that aircraft which are currently being designed or are in the early stages of development would undoubtedly require fuel system and/or combustion system changes if there is a significant change to JP-5 properties during the 1980's or 1990's. There will be new demands on the middle

distillate fraction when the Air Force switches to JP-8 and with the increased use of Diesel engines in automobiles. Unless we receive a Presidential exemption for pollution from military aircraft, we will have to redesign the combustion systems of all our current aircraft. NASA has shown by their clean combustor program that significant combustor redesign will be required to meet the EPA limits using current day fuels. If the future fuels have higher aromatics content and higher end point temperatures, additional combustor redesign may be required. No doubt there are other considerations that I have overlooked, but the future for the aircraft and fuel relationship looks like it could be very complicated.

Our business is fuel development and in that regard we have to reexamine the significant fuel performance requirements that relate to fuel availability from all aspects - aircraft requirements, component and bench test performance, and physical and chemical properties. Figure 2 shows the critical fuel characteristics associated with aircraft, storage and cleanliness requirements. Our task is to assure that we have established the minimum specification requirements for all of these characteristics. In figure 3, we relate the critical fuel properties that are affected by increasing fuel availability through greater distillation range and hydrocarbon composition allowable. As we change the distillation range, the effect of the fuel properties is both good and bad as shown in figure 4. In order to maintain the 140°F flash point of JP-5 we cannot decrease the initial boiling point. By increasing the end point temperature, we detrimentally affect combustion

characteristics, freeze point and viscosity. To further investigate the effect on current fuel availability, a survey was conducted to determine the fuel properties which most affect availability. The results for JP-5 are shown in figure 5. Of the three properties shown, only freeze point and distillation end point can be considered as we are locked into the current flash point limit due to aircraft carrier operation. It points the direction however for future fuel/aircraft development.

The fuels research work approach, shown in figure 6, is to ultimately develop the basic relationships between fuel composition and fuel performance. Once these relationships are established, we will have a better understanding of fuel performance and be able to provide improved definition in specifications as well as a minimum number of requirements. An example of such progress is in the combustion characteristics of fuels. Whereas we have used smoke point, smoke volatility index, and luminometer number as measures of combustion properties, after considerable combustor testing and fuel analysis, we are beginning to standardize on hydrogen content as the single measurement representative of combustion properties. These compositional measurements can be made very accurately and will provide the tools to improve the definition of the fuel specification. Such better definition will allow a more accurate representation of the trade off studies which will be required in the future. As shown in figure 7,

once we have established the minimum fuel requirements, then fuel cost and availability versus increased aircraft weight, complexity, maintenance and cost factors will have to be weighed. If we in the fuels community do our job properly, we will have provided much of the decision making material required to assess this complex situation.

PRESSURES ON AIRCRAFT/FUEL RELATIONSHIP

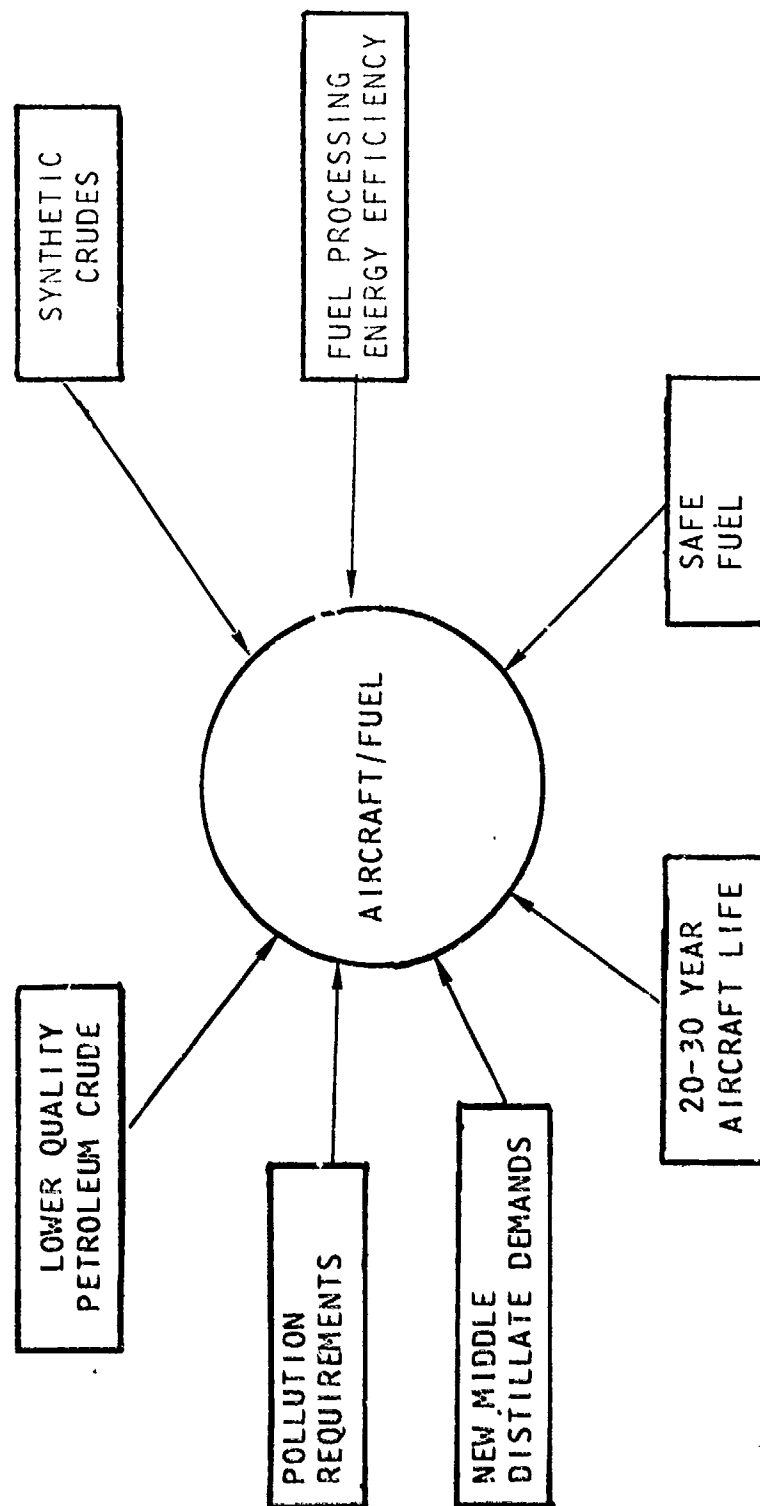


FIGURE 1

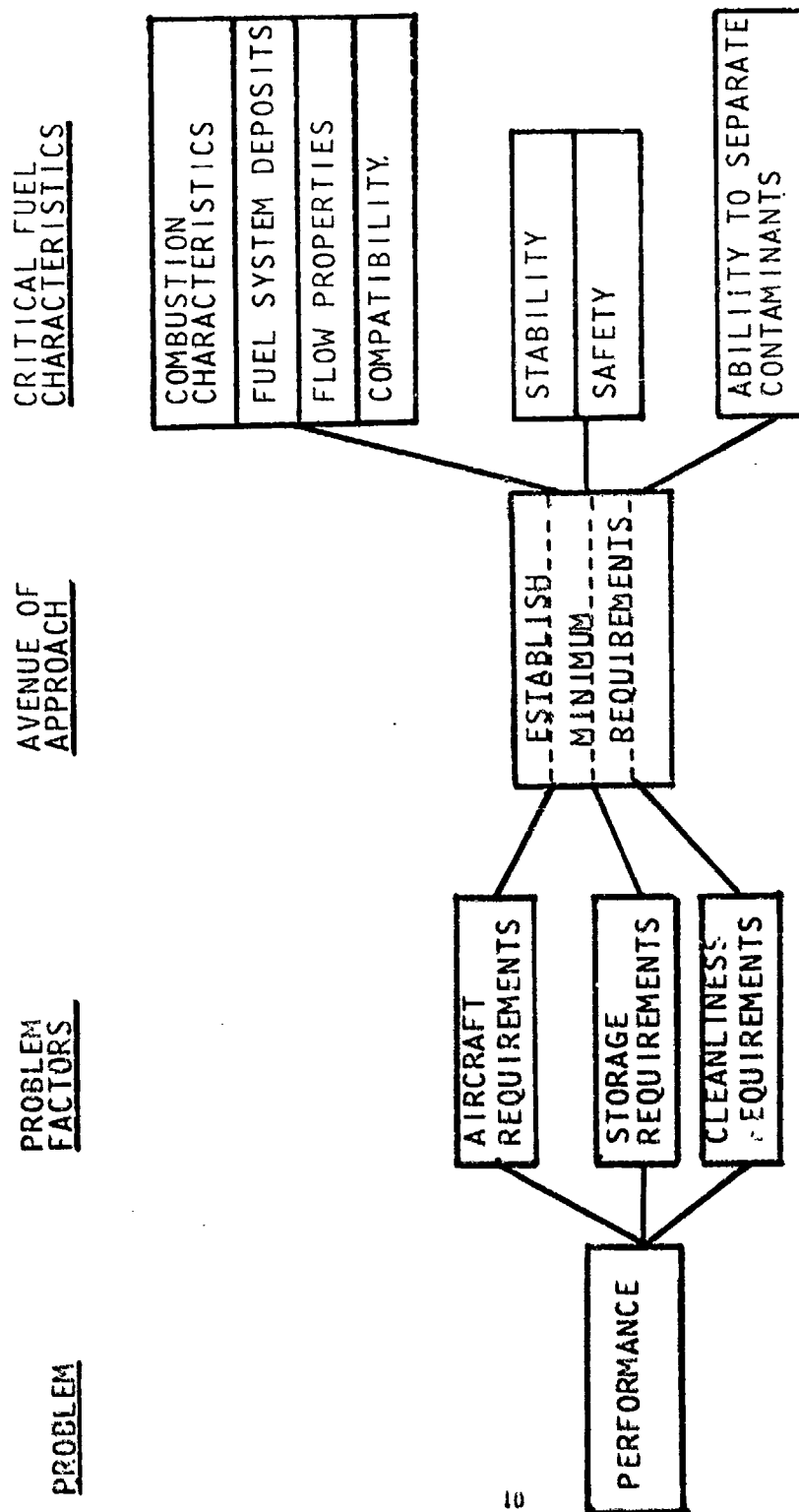


FIGURE 2

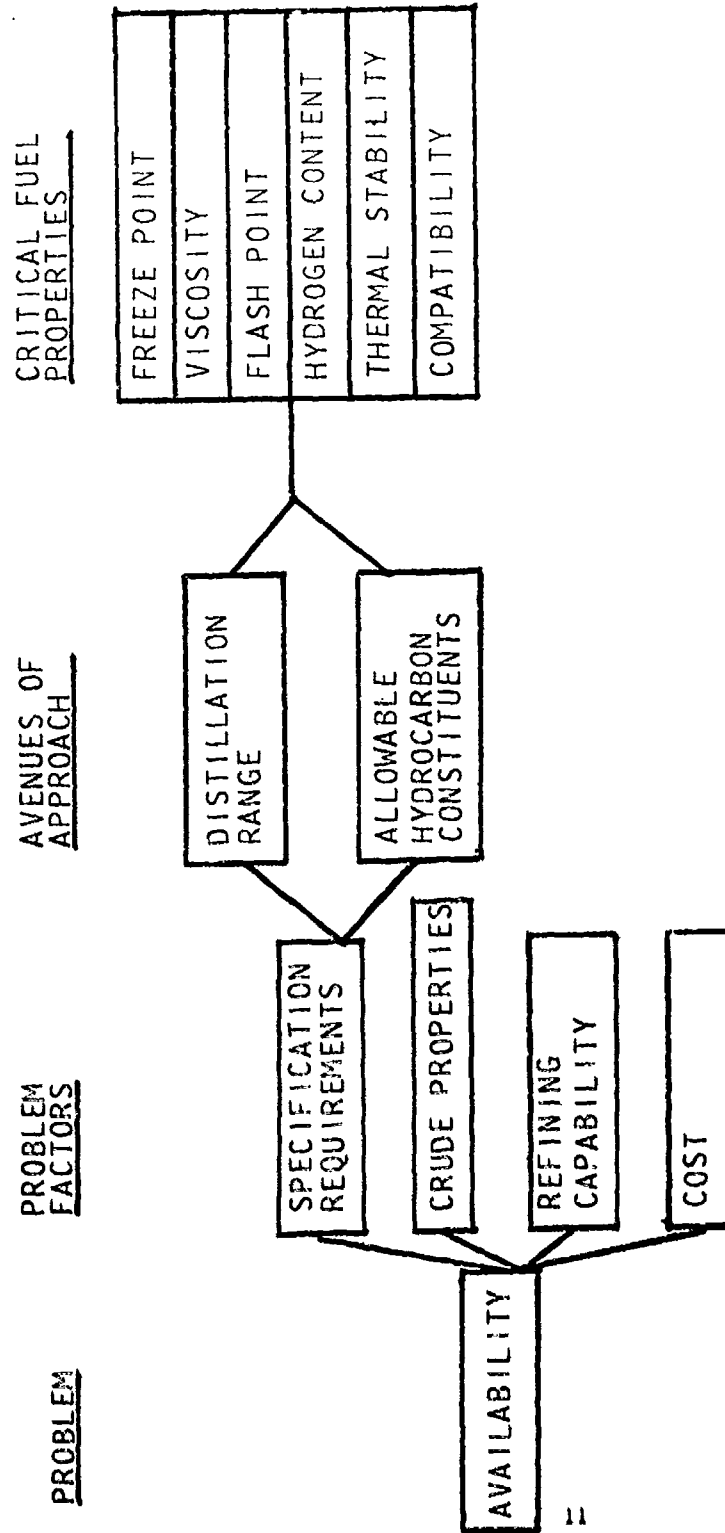
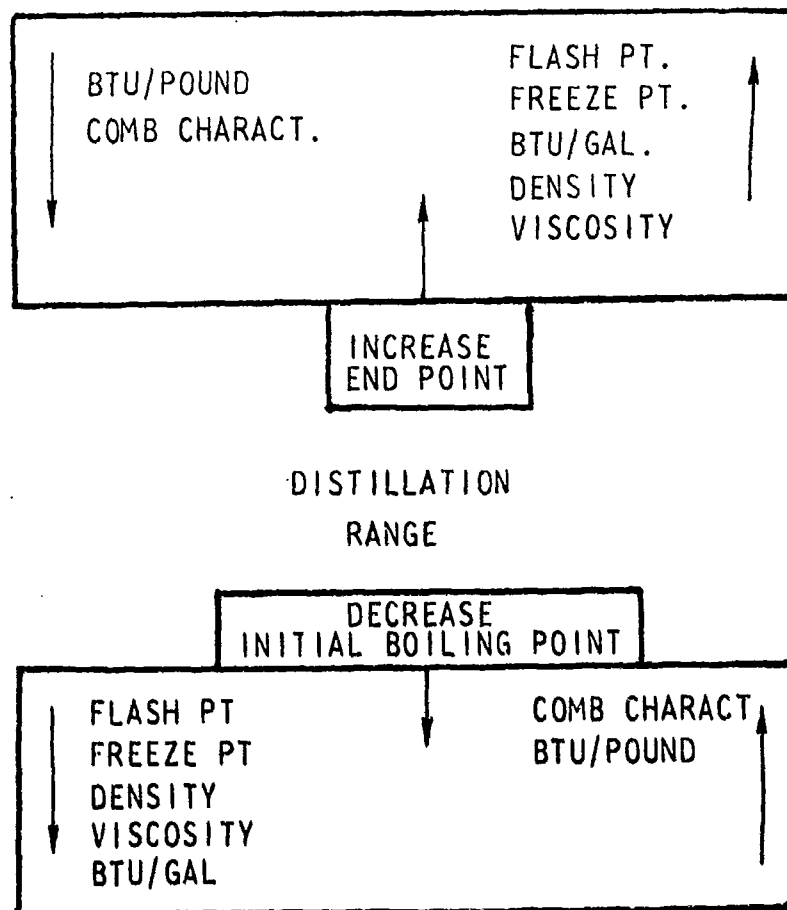


FIGURE 3

SPECIFICATION PROPERTY RELATIONSHIPS



INCREASED FUEL AVAILABILITY

INCREASED AVAILABILITY, %

FUEL PROPERTY

CHANGE BY

FREEZE POINT

+15° F

11.5

2

DISTILLATION END POINT

+25° F

8.3

FLASH POINT

-5° F

3.0

FIGURE 5

APPROACH TO FUEL PROPERTIES INVESTIGATION

HARDWARE TESTS TO ESTABLISH FUEL PROPERTY/PERFORMANCE RELATIONSHIPS

CHEMICAL R&D TO ESTABLISH FUEL COMPOSITION/PROPERTY RELATIONSHIPS

DEVELOP BASIC RELATIONSHIP FROM WHICH MINIMUM SPEC REQUIREMENT CAN
BE ESTABLISHED.

FIGURE 6

AIRCRAFT PERFORMANCE/FUEL QUALITY TRADE OFF

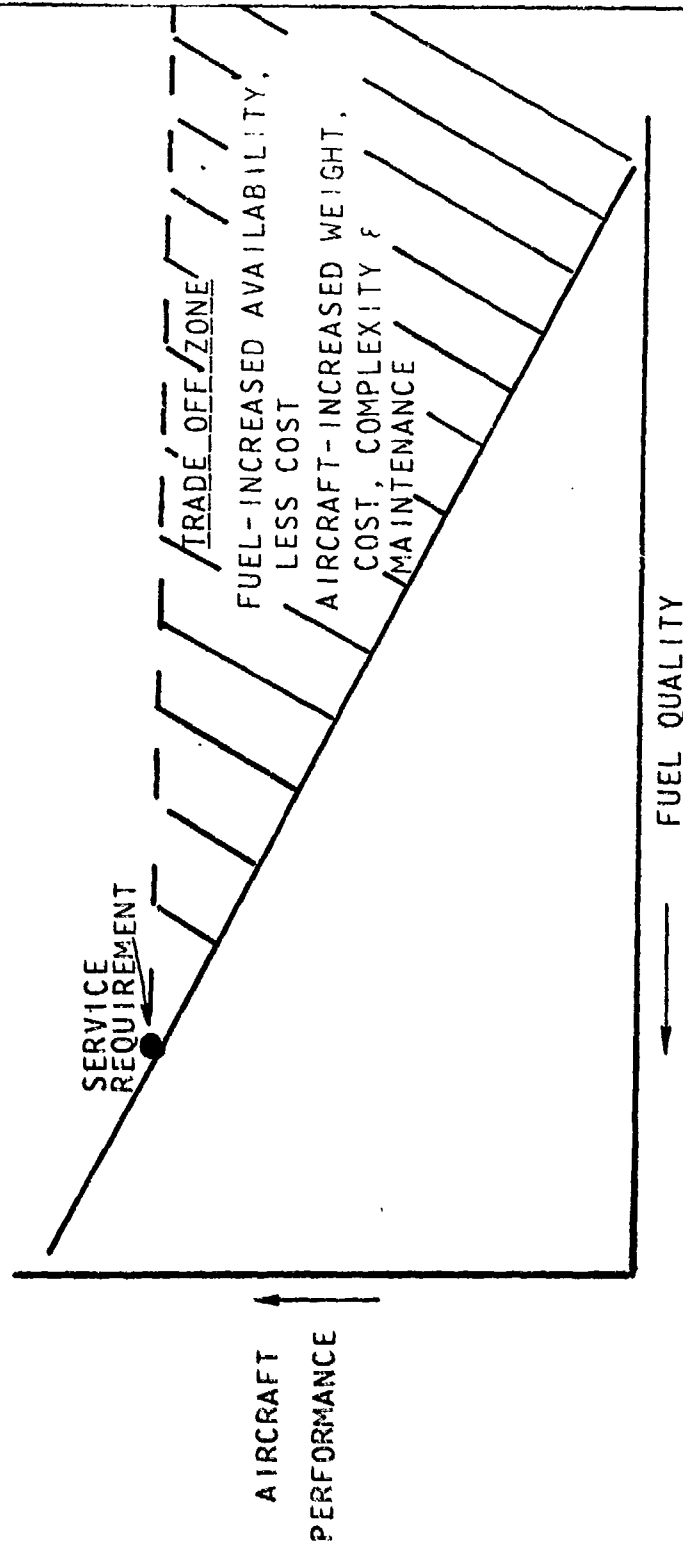


FIGURE 7

SHALE OIL II - UPDATE

LCDR LARRY LUKENS
NAVAL MATERIAL COMMAND

I. OPENING REMARKS

I would like to start by expressing my personal thanks to Dr. Bob Hazlett for inviting the Navy Energy and Natural Resources R&D Office, Naval Material Command, to participate in this important workshop. In the years ahead, I am quite certain that we will be depending upon you, the members of the scientific and engineering communities, to come up with an ever increasing number of solutions to an ever increasing number of problems - problems which we will inevitably face as we enter a period that future historians will likely label as the beginning of the end of the petroleum era. We must transition from our traditional dependence upon conventional petroleum to alternate sources of supply. The basic research needs that workshops such as this define must be provided for if we are to make that transition smoothly -- if at all.

Having been in the energy R&D business for some five years has afforded me the opportunity to follow the energy debate since the early days of Project Independence. It's been a debate that has been waged at virtually every level of our society,

from the man on the street to Capitol Hill. And yet, despite all the words that have been said and written, and despite the fact that the President has declared the Moral Equivalent of War on the energy problem, recent polls indicate that the American public has yet to fully recognize the nature and extent of the energy problem. They have yet to recognize that we now import nearly half of our petroleum requirements; they have yet to recognize that, given recent trends in domestic petroleum production and energy use, our dependence upon foreign oil will continue to rise for the foreseeable future; and they have yet to recognize the effect of these growing imports on the basic economic health and security of the Nation. Perhaps their failure to recognize these facts and trends stems from a lack of understanding - an understanding of the patterns of world petroleum reserves, production, and distribution; an understanding of the importance of the Persian Gulf, particularly in light of the mounting Soviet influence in that region of the World; and an understanding of the vulnerability of these petroleum supply lines which carry an ever increasing level of tanker traffic from the Middle East to the shores of the U.S. and to the shores of our major allies. Perhaps even less understood is the economic and social climate of the OPEC cartel, whereby their ability to produce oil to meet the world demand far exceeds their revenue requirements for domestic spending.

My intent here is not to point the finger, but simply to point out that my engineering background tells me that the solution to any problem normally requires, first of all, defining the problem, and defining the problem normally requires that it first be recognized. On the subject of energy, the polls clearly indicate that on the subject of energy we as a Nation have a way to go.

Taken in the context of the national defense, however, I would like to believe that we are a bit further along.

"There is no more serious threat to the long term security of the United States and to its allies than that which stems from the growing deficiency of secure and assured energy resources"

Certainly the above statement by Defense Secretary Brown, as expanded upon by this mornings' speakers, provides clear evidence that at least we recognize the energy problem and are attempting to define its current and future impact on our ability to provide for the national defense. So much for problem recognition and definition - how about the solution.

II. ALTERNATIVES TO CONVENTIONAL MOBILITY FUELS

Taken in the national perspective, two basic energy solving approaches have emerged. On the one hand are the so-called "energy liberals" advocating the so-called "soft" approach, meaning a small, decentralized, largely solar-based energy supply system. On the other hand are the so-called "energy conservatives" advocating the so-called "hard" approach, meaning basically a continuation of our existing centralized energy

supply systems with greater emphasis on nuclear power. As has been the case, historically, with most polar issues, our eventual energy path will no doubt follow some intermediate course between the hard and soft approaches. As the dust starts to settle on the hard versus soft energy debate, however, a basic recognition of the facts will inevitably emerge - Alvin Weinberg, in his recent article in the American Scientist, called these facts, "Thermodynamic Imperatives." I'm certain that you didn't come here to get a lecture on classical thermodynamics, so stated simply these imperatives are:

(1) Since energy is conserved, we are not dealing with a shortage of energy, but a shortage of energy in useful form. In this context, we have succeeded in nearly exhausting the more traditional energy forms, such as oil and natural gas, and are now faced with the prospect of converting lower availability forms of energy, such as coal, into forms required of present day systems.

(2) Conservation of energy makes good sense but can only be counted on to head off the inevitable supply problem - not solve it.

By way of comparison, there are certain imperatives, thermodynamic and otherwise, that will impact upon the energy problem as it relates to national defense. The most significant of these imperatives is our continuing dependence

upon liquid hydrocarbons to satisfy our defense mobility fuel requirements. It is highly unlikely, if not virtually impossible, that we will be able to sever our dependence on liquid hydrocarbon fuels, particularly for ships and aircraft, for the next quarter to half century - the same time frame within which conventional petroleum sources will be virtually exhausted. We must find alternatives - alternatives which are domestically controllable, technically feasible, and economically, environmentally, and socially acceptable.

For the near term, say for the next half century or so, those alternatives for liquid hydrocarbons transportation fuels will find their genesis in various fossil energy forms. The problem, of course, is that to make this a practical reality, we must convert the lower availability forms, such as coal and oil shale, to the higher availability forms required of our present day systems, particularly as required for the transportation industry and particularly as required by our mobile defense systems. For the production of transportation fuels, each of these fossil energy sources pose certain advantages and disadvantages.

While coal offers one of the greatest potentials for relieving our ever growing dependence upon imported oil, the U.S. technology for producing liquid fuels from coal is lagging that of other alternatives, particularly oil shale.

Moreover, because of the high degree of costly hydrotreating required to bring coal liquids into the middle distillate fuels range, economic considerations will most likely direct liquid products derived from coal towards the gasoline, boiler heating oil, and petrochemical feedstock markets. Accordingly, further consideration of coal derived defense mobility fuels must necessarily await further advances in coal processing technologies leading to the commercial availability of the middle distillate fuels of primary interest to the military.

From a technical viewpoint, tar sands represent a potentially viable source of middle distillate range defense mobility fuels. However, the relatively small extent of the U.S. tar sand deposits and the lack of any significant national effort to develop these deposits precludes serious consideration of this alternative, at least for the immediate future.

Of the various fossil energy alternatives to petroleum, oil shale must be considered the most attractive near term source of defense mobility fuels. Within the U.S., several oil shale extraction technologies have been developed and tested in equipment ranging from one-tenth to one-fourth commercial size. Compared to other synthetic sources of liquid hydrocarbon fuels, oil shale appears to be more economically viable; however, not sufficiently viable to date to muster the required private investor interest to commercially develop this important resource.

III. OIL SHALE

Oil shale is a fine-grained sedimentary rock which contains an insoluble organic material, called kerogen, which will yield oil, gases, and residual carbon when destructively decomposed under the influence of heat. The kerogen in oil shale is a complex molecular material composed primarily of carbon, hydrogen, oxygen, sulfur, and nitrogen.

Oil shale is typically found in geological basins, wherein the rock formations consist of layers of kerogen sandwiched between layers of sedimentary rock. Lower grade, shallow deposits of oil shale underlie large areas of the eastern and central United States and northern Alaska. The higher grade deposits are those that occur in what is known as the Green River Formation underlying some 16,500 square miles of Colorado, Utah, and Wyoming.

Approximately 50 to 60 million years ago, two large tertiary lakes existed in the intermountain basins of northwest Colorado, northeast Utah, and southwest Wyoming. Over a period of some 10 to 12 million years, sediments rich in organic matter were deposited in these lakes and, under oxygen deficient conditions, formed the oil shale deposits of the Green River Formation. Within this formation, the Piceance Creek Basin in Colorado contains 85 percent of the richer shale deposits. These beds of shale range from 100 to 2000 feet thick, lying 100 feet below the surface at the edge of the basin to over 1000 feet

below the surface at the center of the basin. The remainder of the high grade shale is located in the Uintah Basin in Utah (10 percent) and in the Green River Basin in Wyoming (5 percent).

Of the total U.S. deposits of oil shale, those of the Green River Formation are considered to be the more commercially attractive.

This formation has a known resource of 570-620 billion barrels contained in 25-100 gallon per ton shale, 1,430 billion barrels contained in 10-25 gallon per ton shale, and 2,000 billion barrels contained in 5-10 gallon per ton shale. Recent estimates indicate that approximately 600 billion barrels of the richer grade shales could eventually be classified as reserves given proven commercial scale technologies and improved economic conditions. For purposes of comparison, the free world's proven crude oil reserves as of January 1978 totalled 548 billion barrels and the U.S. presently consumes approximately 6 billion barrels of petroleum products annually.

There are two basic approaches to extracting oil, or kerogen, from oil shale: surface retorting and in-situ retorting. Historically, the surface retorting approach has had the benefit of more time, effort, and dollars, as result of which several proprietary technologies have emerged in recent years. They all represent variations of the same

retorting scheme, each offers certain advantages and disadvantages, and each has been demonstrated at the pilot and/or semi-works scale. What remains to be proven is how well these various surface retorting technologies work in commercial scale equipment.

There are two basic approaches to in-situ retorting: true in-situ and modified in-situ. Of the two technologies, the modified in-situ approach is far more advanced. As in the case of surface retorting, several companies have been experimenting with various proprietary techniques. Once again, each has its advantages and disadvantages and, again none has been suitably demonstrated on a commercial scale.

How well these technologies work in terms of service factor, percentage yields of gas and oil, thermal efficiency, water requirements, spent shale disposal, etc. are important considerations that will have a significant impact on the economics and the environmental impact of commercial scale operations.

A comparison between surface and in-situ retorting techniques again offers an interesting contrast of advantages and disadvantages. Generally, surface retorts have the advantage of greater control over the retorting process, which in turn provides for more reliable service factors and higher yields of oil and gas. Chief among the disadvantages of surface retorts is the large scale of mining and materials

handling required and spent, or retorted, shale disposal. Generally, just the opposite is true in the case of in-situ retorting.

For reasons of maximum resource recovery and, accordingly, improved economics, the first generation of commercial shale oil recovery plants in the U.S. will likely use a combination of surface and modified in-situ retorting technologies.

With regard to the conversion of shale oil into refined petroleum products, it is generally recognized throughout the refining industry that, economics aside, present state-of-the-art refining technology will be adequate for the processing of whole crude shale oil into a slate of suitable end fuel products. It is further recognized, however, that there is a need to improve the economics of refining shale oil in order to bring the cost of shale-derived fuels into a competitive status with the price of conventional fuels. To achieve this competitive economic status for a shale oil refining industry will obviously require some research effort directed towards the optimization of refining methods specifically tailored to shale oil processing requirements. In this regard, it has been clearly demonstrated throughout the history of the refining industry that improvements in the economics of refining are strongly influenced by the physical and chemical properties of the crude feed stock and by the market within which the end slate of products are to be

distributed. Accordingly, any research effort directed towards the development of optimized refining techniques must clearly identify at the outset the nature of the refinery feedstock and the requirements of the market place which is being targeted for product distribution.

As with refining, the end-use testing of shale derived fuels is not considered a major technical barrier to oil shale development. Demonstrating the suitability of shale derived fuels in various end-use systems is, nonetheless, of importance to establishing the overall economics of this growth industry. With respect to the DOD interest, however, it is essential that the suitability of shale derived fuels for military use be fully assessed before the Armed Forces will be prepared to acquire and use these fuels at the time they become available in commercial quantities.

IV. NAVY SYNTHETIC FUELS R&D PROGRAM

The most significant Navy R&D programs to date in this area have been involved with the acquisition, refining, and test and evaluation of synthetic fuels derived from oil shale. These activities have focused upon the utilization of the Naval Oil Shale Reserves as a potentially viable source of military specification fuels.

In 1974 the Navy served as the lead agency for a joint DOD, ERDA, NASA, Coast Guard, and MARAD project to refine and test fuels derived from 10,000 barrels of crude shale oil produced

by the Paraho process. Under this joint agency program coordinated by the Navy, approximately 10,000 barrels of crude shale oil produced in the Paraho 8 1/2 foot semi-works plant at Anvil Points were shipped to the Gary Western Refinery to be processed into seven different military and commercial fuels. The fuel types produced were gasoline, JP-4, JP-5/JET A, DFM/DF-2 and heavy fuel oil.

These fuels were then tested at various government and industry laboratories. These series of tests culminated in the successful operational flight of a T-39 jet aircraft by the Air Force, the successful operational cruise of the Great Lakes steamer, Edward B. Green, sponsored by the Navy, MARAD, and the Coast Guard; and the operational testing of a jeep (L-141) engine by the Army. The majority of the fuels produced, however, exhibited certain physical and chemical property deficiencies. Generally, these deficiencies were in the areas of high gum and wax content, high concentrations of fuel-bound nitrogen, and poor thermal and storage stability, all of which can be attributed to the refining process used. Aside from these deficiencies, these tests clearly demonstrated the feasibility of using crude shale oil as a feedstock for military fuels, particularly those in the middle-distillate range (jet and marine fuels).

As a follow-on to the previously conducted 10,000 bbl shale oil refining/testing program, the Navy is presently serving

as the contracting agency and project director for a joint DOD/DOE program for the acquisition, refining, and testing of fuels derived from 100,000 bbl of shale oil produced by the Paraho process on the Naval Oil Shale Reserves near Rifle, Colorado. Under the present schedule the refined military fuels from this project will be available in January 1979 for test and evaluation.

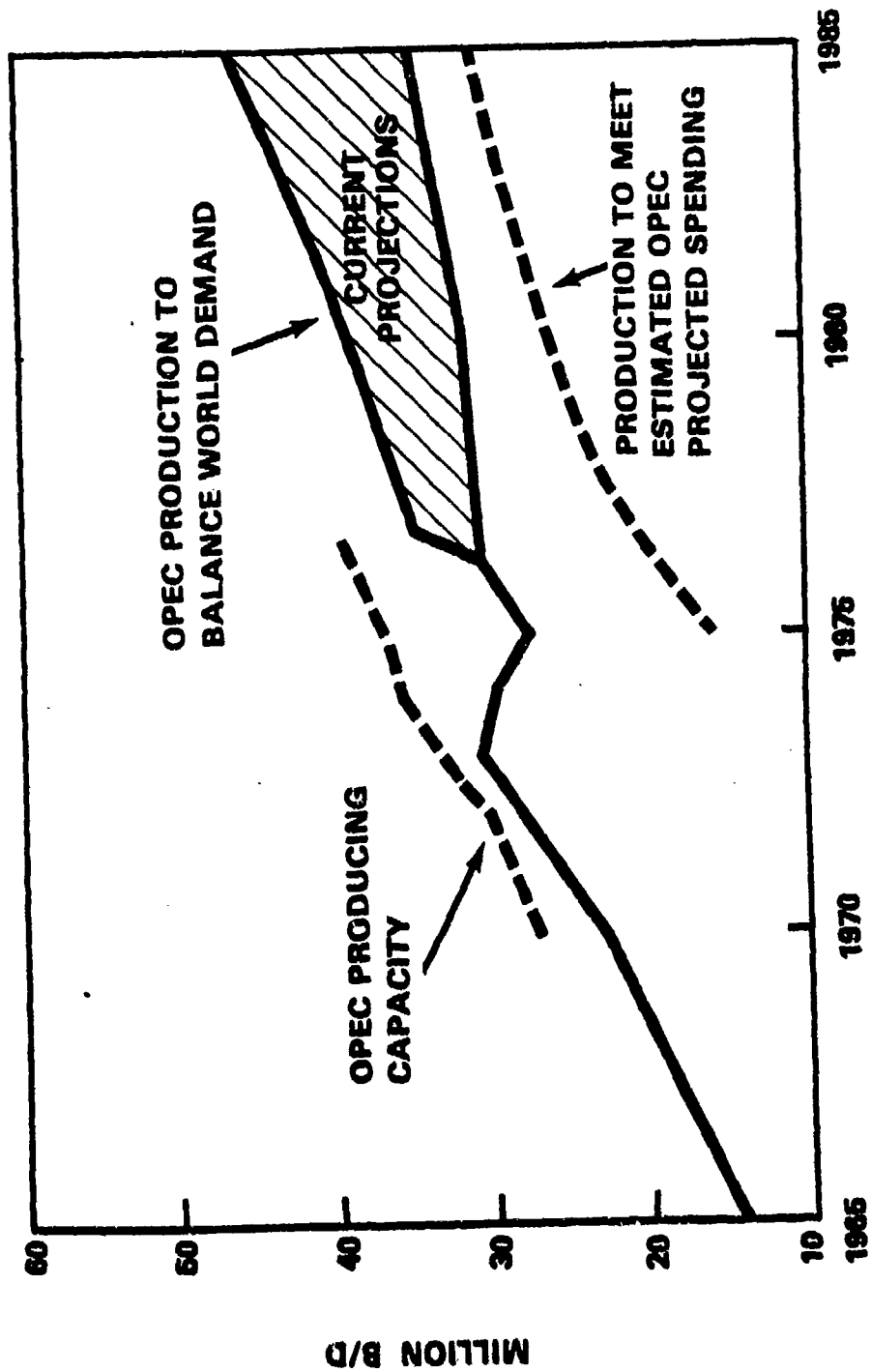
As has been the case in the past, DOD's future plans should continue to be based upon the philosophy of adapting various emerging synthetic fuels technologies to specific military requirements in a manner which is totally supportive of and which receives maximum benefit from the National Energy Program. With this philosophy in mind, detailed discussions are on-going between the Navy, DOD, and DOE officials with respect to the planning and execution of follow-on syncrude acquisition, refining, and synfuels testing programs. The continuation of this dialogue and joint agency planning will be mutually beneficial. DOE will benefit from DOD testing of synfuels in support of their various national demonstration programs. DOD will benefit from the experience gained in assessing the suitability of synfuels for military use and will therefore be prepared to use these fuels at the time they become commercially available.

It is imperative that the ultimate objective of DOD's efforts in synthetic fuels be directed towards minimizing the potential loss of military effectiveness that would inevitably result from a disruption of energy supplied

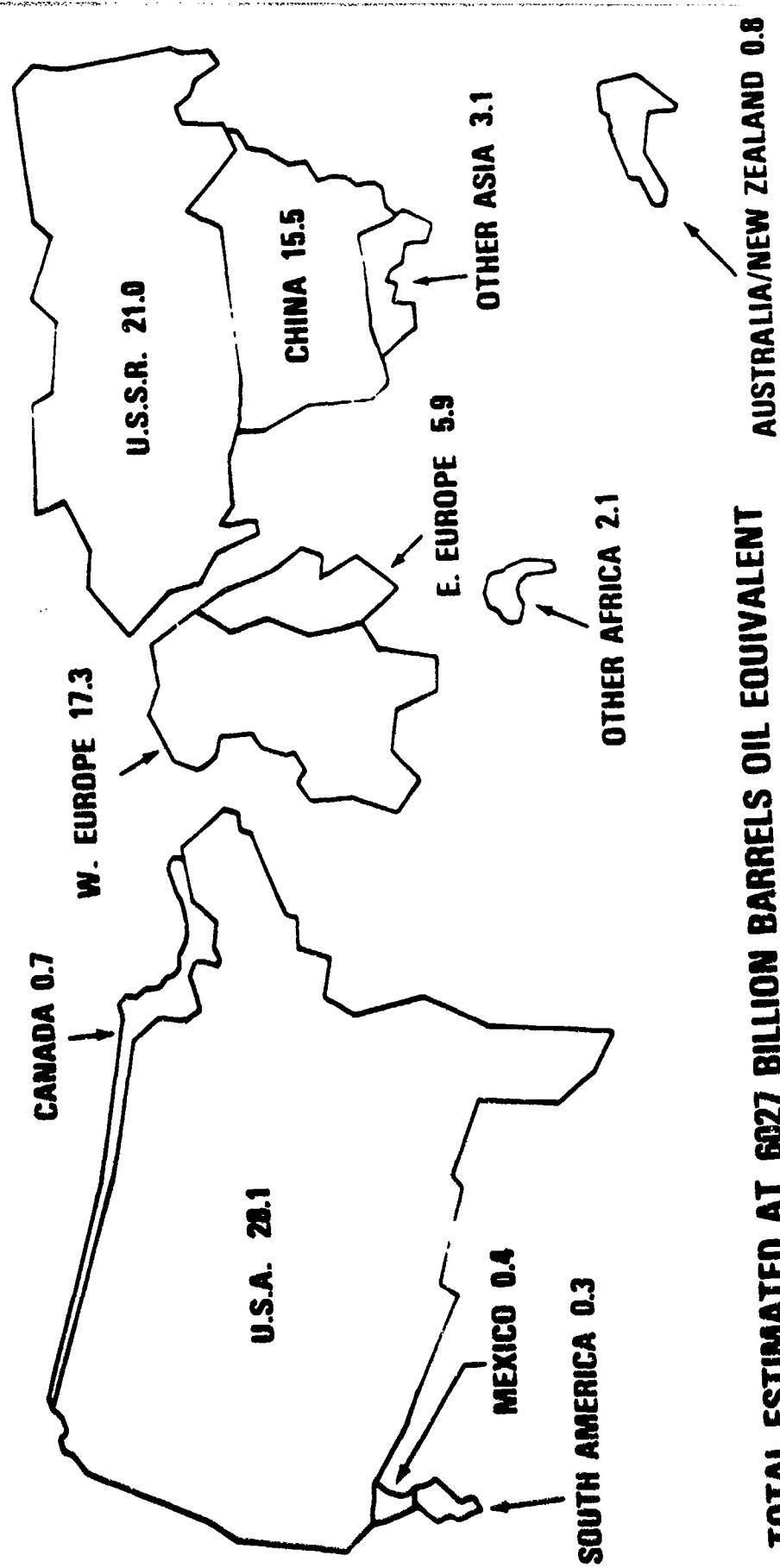
under foreign control. This objective can best be met by placing the DOD in the position of an informed customer for the fuels produced by the emerging commercial synfuel industry. The various synfuel programs now underway with the Navy, as well as those planned for the future, are specifically designed for this purpose.

In summary our various R&D efforts are directed towards assessing the suitability of synthetic fuels for DOD use, with early emphasis on oil shale. Our final products from this R&D effort will be fuel procurement specifications and end use guidelines for the operating forces. If we do our job right, we will contribute towards ensuring that our energy supply lines remain full, providing energy to the Armed Forces in the right form, in the right place and in sufficient quantities to carry out our missions around the World.

WORLD DEMAND MAY EXCEED OPEC NEED TO PRODUCE

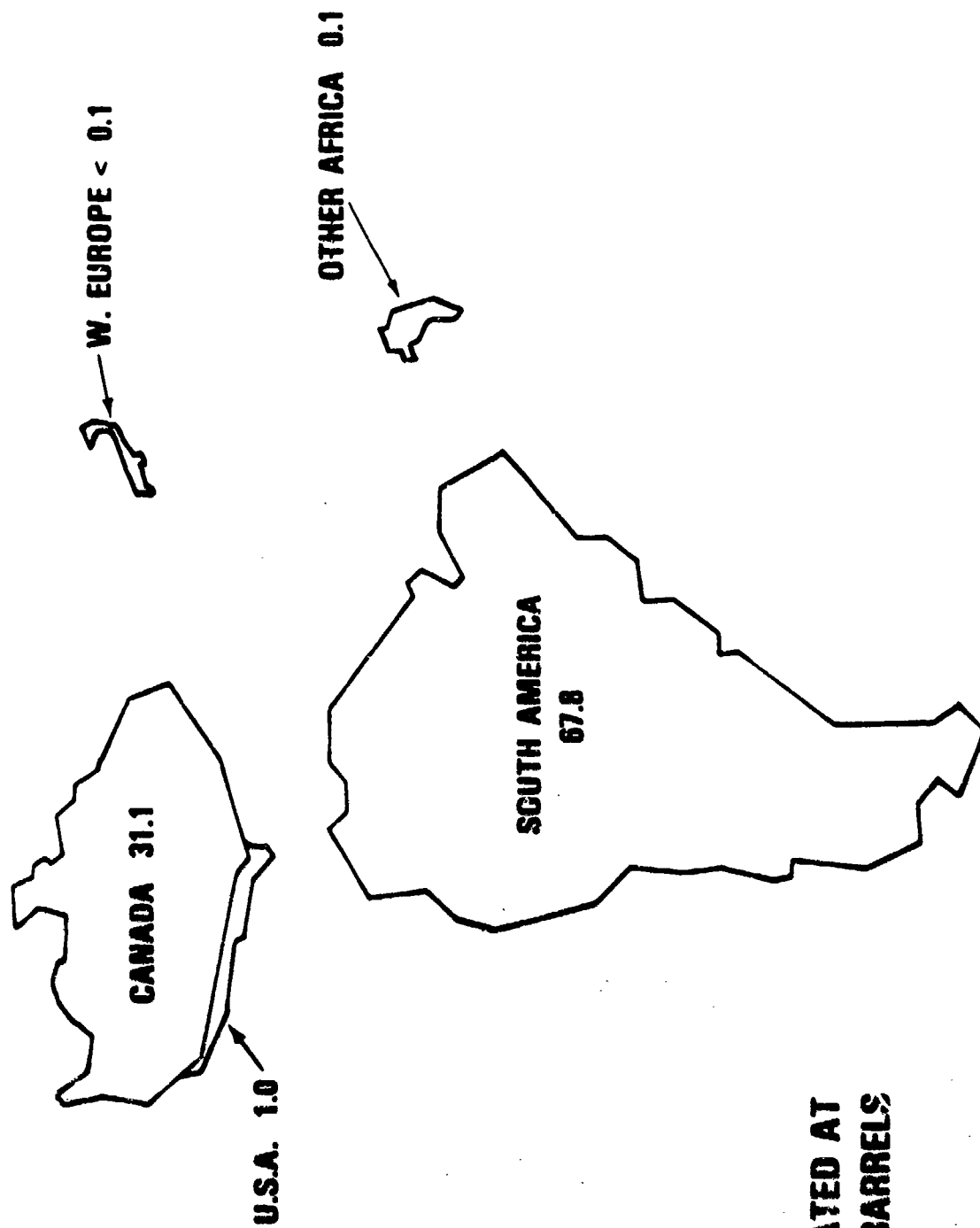


WORLD COAL RESERVES (PERCENT)



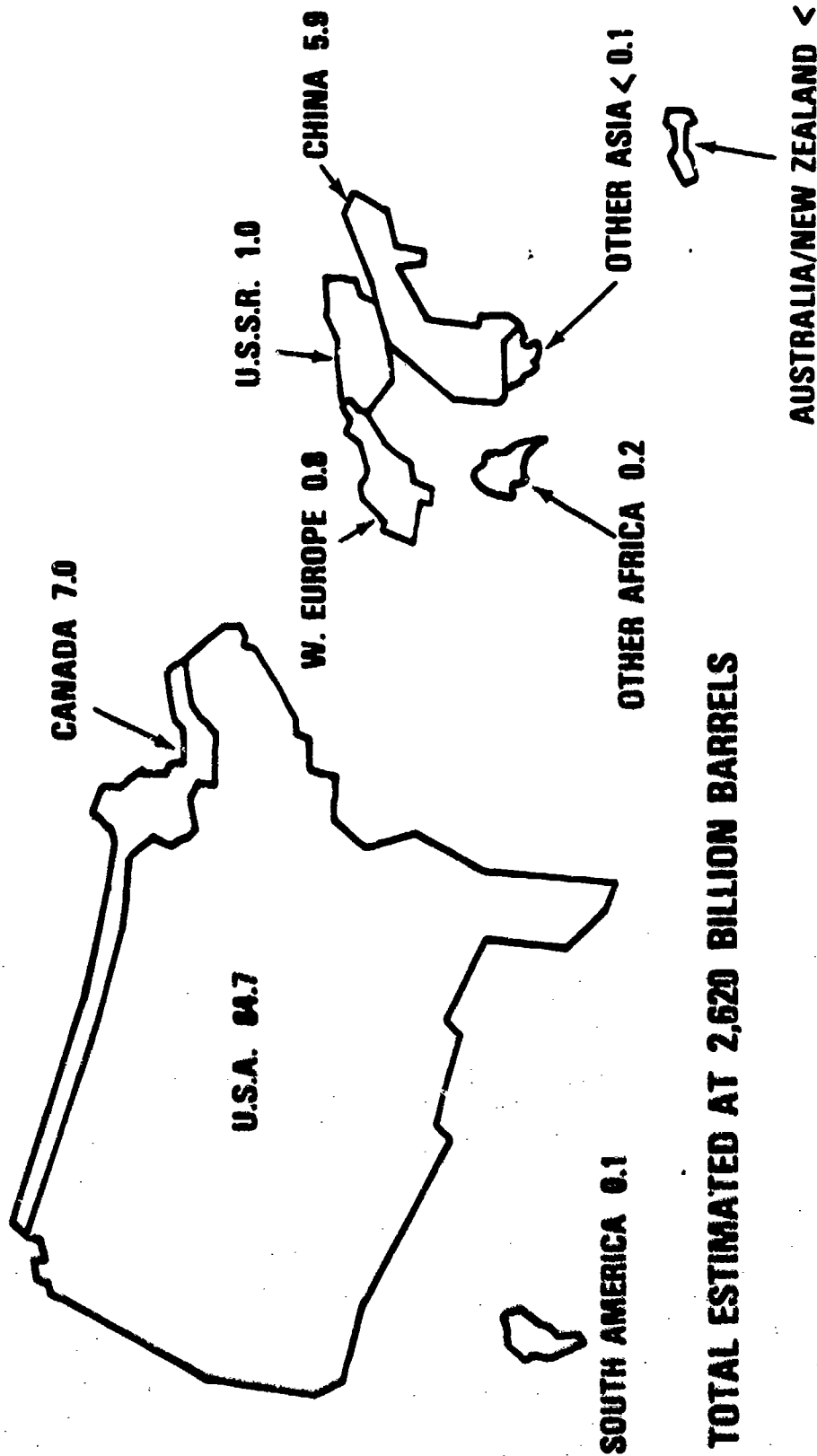
TOTAL ESTIMATED AT 6027 BILLION BARRELS OIL EQUIVALENT

WORLD TAR SANDS RESOURCES (PERCENT)

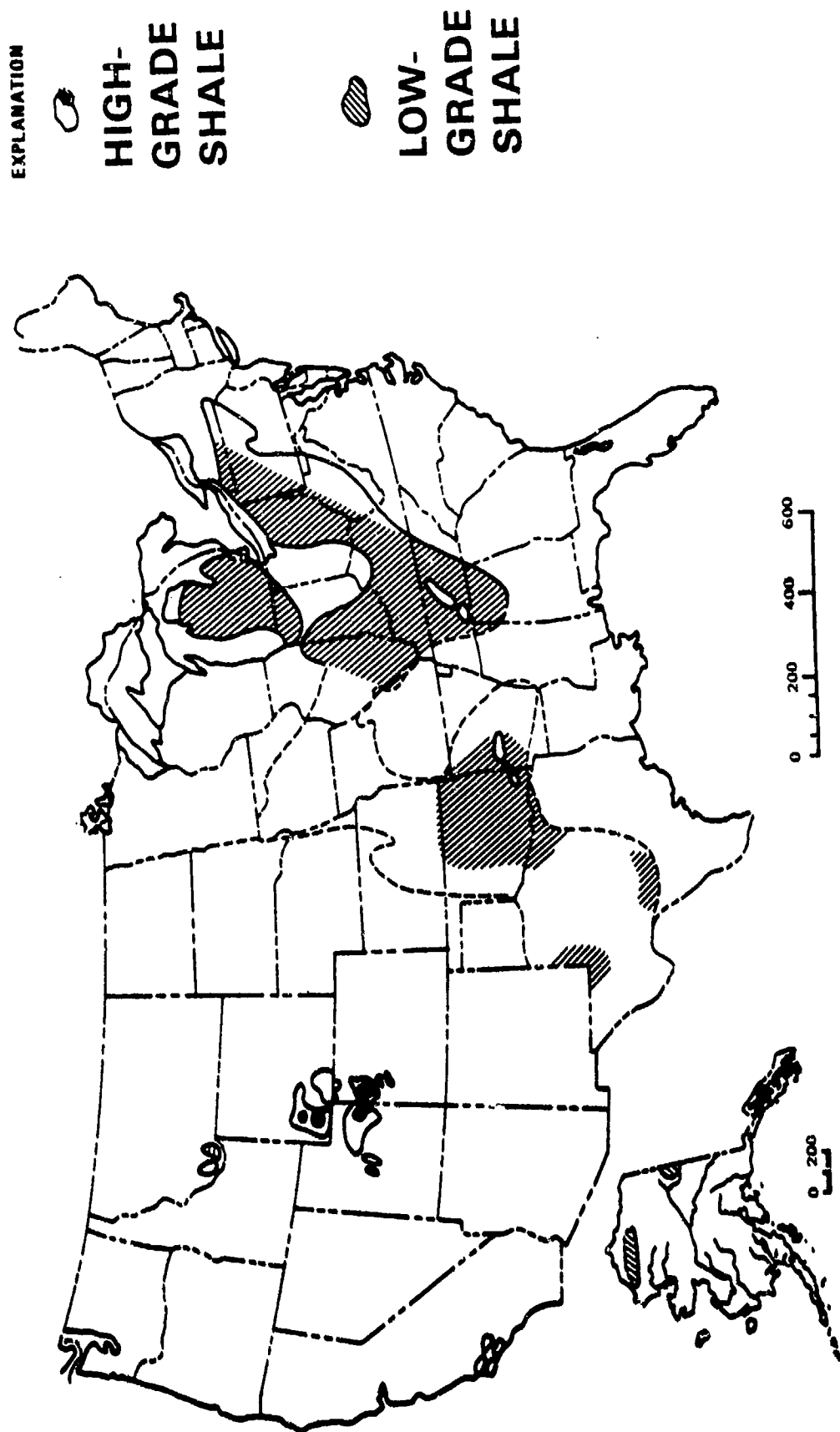


TOTAL ESTIMATED AT
2877 BILLION BARRELS

WORLD OIL SHALE RESOURCES (PERCENT)



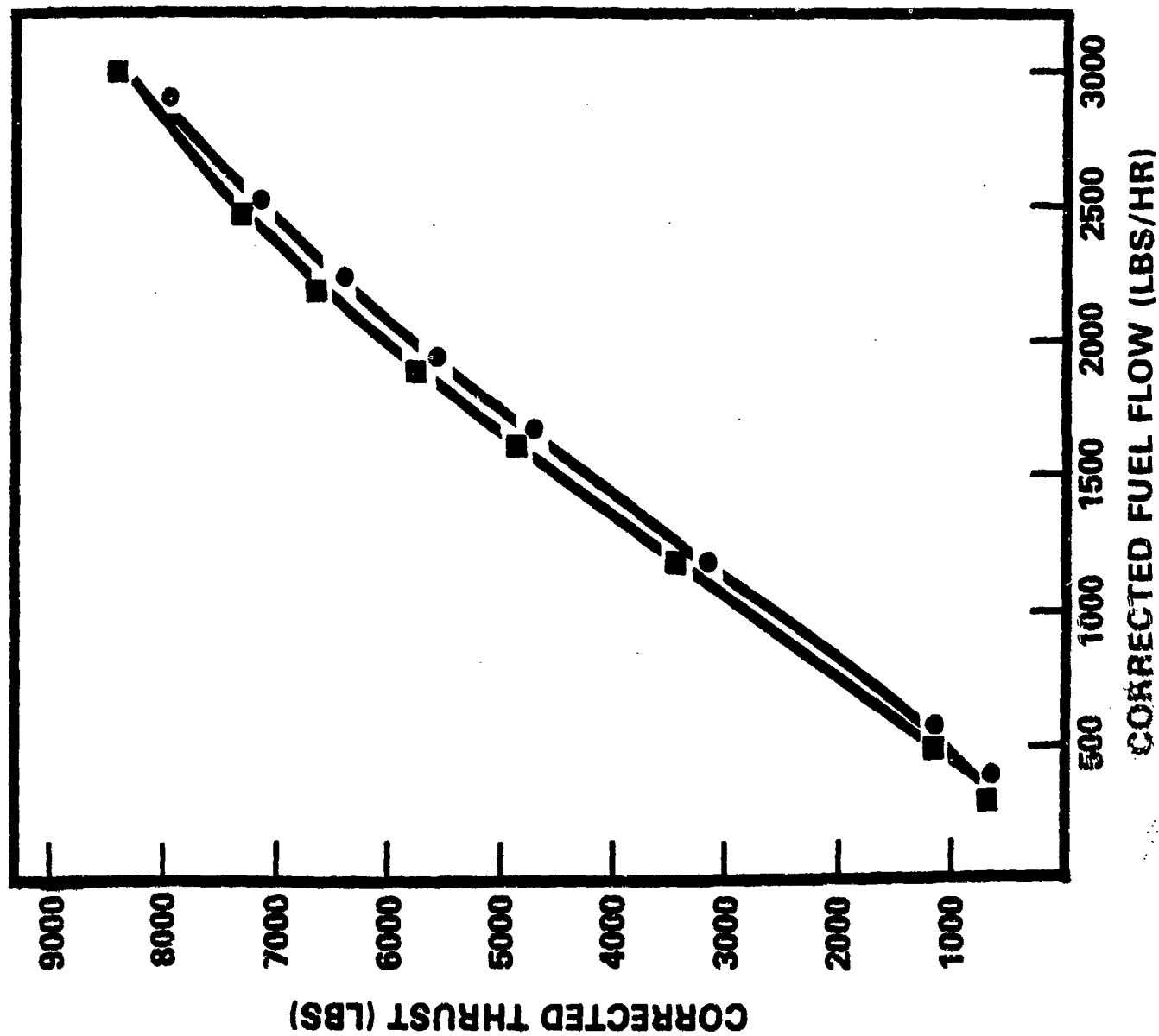
PRINCIPAL REPORTED OIL-SHALE DEPOSITS OF THE UNITED STATES



SHALE OIL PERFORMANCE CORRECTED TO STANDARD DAY CONDITIONS

LEGEND

- PETROLEUM JP-5
- SHALE JP-5



SHALE OIL II
PILOT PLANT REFINING STUDIES

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Introduction

The purpose of this paper is to present the results of the Phase I portion of the U.S. Navy's program to refine up to 100,000 barrels of Paraho shale oil into military fuels. The paper will cover the following topics:

Background
Pilot Plant Program
Refining Program
Conclusions

Pilot Plant studies were performed by Sohio
under Navy Contract N00014-77-C-0750

Background

In 1975, the Navy sponsored a program to produce and refine 10,000 barrels of Paraho shale oil into military fuels. Sohio performed the preprocessing studies and the refining was done at Gary Western's refinery in Fruita, Colorado. The following products were produced from this run:

Gasoline	725 barrels
JP-4	454 barrels
JP-5/Jet A	650 barrels
DFM/DF2	1965 barrels
Heavy Fuel	2760 barrels
Coke	212 tons

These fuels met a majority of the standard specification requirements, and demonstrated the feasibility of using crude shale oil as a feed stock for military fuels. However, the fuels were not thermally stable, had high gum, wax, and nitrogen contents.

As follow-up to the Gary Western refining run, the Navy is now conducting experiments directed toward acquisition and refining of up to 100,000 barrels of Paraho shale oil, with the objective of producing the highest possible yield of military specification fuels. Sohio is performing this work for the Navy under a subcontract with the Paraho Development Corporation. This refining program is being conducted in two phases. Phase I provides for the development and demonstration, in suitable pilot plant facilities, of refining methods and operating conditions for producing military specification fuels from Paraho shale oil. The second phase would be the actual refining run.

In developing the approach to the Navy program, Sohio considered the following factors:

1. Shale oil characteristics
2. What would be a feasible commercial approach to refining Paraho shale oil?
3. What refining facilities could Sohio make available to refine 100,000 barrels of Paraho shale oil?
4. What modification to the above process lineup could be made for a demonstration run?

The most significant differences between Paraho shale oil and typical crude oils are:

1. Very high nitrogen levels (~ 2.0 wt%)
2. High oxygen levels (~ 1.2 wt%)
3. Low volume of 650°F minus material (~ 29 vol%)
4. High iron and arsenic levels.

The nitrogen and oxygen levels dictate a higher hydro-processing severity to make stable products. Due to the small yield of 650°F minus material, a significant amount of cracking will be required to increase the yields of jet fuel and DFM. The iron and arsenic will also present catalyst poisoning and pluggage problems in hydrotreating.

For the Gary Western run, coking was the first processing step. This resulted in converting ~ 15 weight per cent of the shale oil into high nitrogen coke.

Coking would solve some of the shale oil pretreatment problems. It would probably eliminate the need for a guard filter to prevent pluggage; however, it would not relieve the

arsenic problem. Coking would also reduce the hydrogen requirement for processing the shale oil. Figure I gives a block flow diagram using coking as the first processing step.

However, the value of the coke would, at best, be fuel value, and have to be discounted to reflect the cost of NO_x control equipment on the burning facilities. Also, after the considerable effort to recover the shale oil as a liquid, converting it back to a low value solid fuel does not seem reasonable, especially in light of the work on attempting to convert coal from a solid fuel to either liquid or gas.

The typical approach to processing crude oils is to feed the crude to a Crude Unit. The Crude Unit is basically a large fractionating tower, which splits the crude into the desired boiling range fractions for product blending or downstream processing. We do not think this would be an efficient approach to processing Paraho shale oil. Less than 30 volume per cent of Paraho shale oil boils below 650°F; therefore over 70 volume per cent of the shale oil would be in the Crude Tower bottoms product. This 650°F plus material will require a severe hydro-treat before feeding to downstream processing (Figure II). The high severity hydrotreat will result in significant hydro-cracking, thus requiring a refractionation of the liquid products. The tower required for this refractionation will be similar to the Crude Tower. The light products from the refractionation will probably need additional hydrotreating to reduce their nitrogen levels, since the lighter products have more stringent stability requirements or require lower nitrogen levels for downstream processing units. The net result of this approach would probably be a higher capital investment, and higher operating costs, with little difference in overall hydroprocessing requirements.

Based on in-house information and outside publications, Sohio has concluded that whole shale oil hydroprocessing is the most viable first step for refining shale oil into military fuels. After fractionation of the hydrotreated shale oil, the products will require some additional processing. The gasoline fraction will require additional hydrotreating to meet reformer feed specifications for the production of motor gasoline. The jet and diesel fuel cuts would also require additional hydrotreating, and possibly clay treating, to meet final stability specifications. The bottoms (650°F plus material) would probably be used as feed to a FCC (Fluid Catalytic Cracker) Unit. Additional gasoline and diesel fuel would be produced from the FCC unit. (See Figure III)

In surveying Sohio's refineries, the Toledo Hydrocracker I unit was the only unit that could be used for processing the shale oil without a major disruption of normal refinery operations. No hydrotreating of individual cuts or reforming of gasoline stocks could be accommodated at Toledo.

In light of the facilities that could be made available, Sohio decided to substitute acid and clay treating for hydrotreating of the jet fuels and DFM. (Figure IV) The gasoline stocks, if the Government so desire, would be sent to a third party for hydrotreating and reforming. The 650°F plus bottoms would go to heavy fuel. To increase jet fuel and DFM yields, we would consider recycling a portion of the 650°F plus bottoms.

Pilot Plant Program

The primary objective of the pilot plant program was to demonstrate the planned processing approach to refining up to 100,000 barrels of Paraho shale oil into military fuels, principally JP-5 and DFM, in such manner as could be duplicated at Toledo Refinery. Also, specified quantities of products would be produced from the pilot plant program for the Government to evaluate. They are:

<u>Product</u>	<u>Specification</u>	<u>Quantity</u>
Aviation Gasoline (100/130)	MIL-G-5572E	1 gallon
Type I Gasoline	MIL-G-3056C	1 gallon
JP-4	MIL-T-5624K with Amendment #1	5 gallons
JP-8	MIL-T-83133	1 gallon
JP-5	MIL-T-5624K with Amendment #1	10 gallons
DFM	MIL-F-16884G	10 gallons
Burner Fuel	VV-F-815C	10 gallons

The pilot plant program included the following:

- Catalyst screening
- Pilot Plant demonstration run
- Product blending
- Product treating

The screening studies were performed in a small pilot plant with a catalyst loading of 200 cc. Past studies on this facility have correlated well with actual plant operations on the Toledo Hydrocracker I unit. The objective of the catalyst screening studies was to determine which catalyst or combination of catalysts would give the best hydrocracking-hydrotreating results. The criterion for selecting the catalyst was the 650°F point on the hydrotreated product, since the jet fuels and DFM would be made from the material boiling below 650°F. Five commercial catalysts were screened at approximately constant space velocity, temperature, and hydrogen partial pressure. The catalyst selected for the demonstration run converted ~65 volume per cent of the shale oil into the 650°F minus fraction with the total nitrogen content of 0.24 weight per cent. The other catalyst results were similar on conversion, but the nitrogen levels were in the range of 0.35 weight per cent. (Due to proprietary agreement, no additional information can be divulged on the screening studies.)

For the demonstration run, a larger pilot plant was used with a reactor volume of 1900 cc. The pilot plant demonstration run was started on normal petroleum feedstock to establish a base point for catalyst performance. The feed was then switched to Paraho shale oil and the unit lined-out at the processing conditions that can be duplicated at Toledo. Space velocity and temperature were in the range used by others for shale oil hydroprocessing; hydrogen partial pressure was lower. After allowing the pilot plant to line-out, part of the 650°F plus bottoms was recycled back to the reaction section. The fresh feed rate was reduced to maintain total feed rate. The pilot plant was operated at the above conditions for 1400 hours to make sufficient material to make the required product sample volumes. The 1400 hours corresponds to processing 200,000 barrels in the Toledo Hydrocracker I unit. The reactor yields for SOR (start-of-run) and EOR (end-of-run) are tabulated in Table I.

After completing the demonstration run at constant processing conditions, the hydrogen partial pressure was increased 500 PSI. The other processing conditions were unchanged. The reactor yields for this operation are tabulated in Table II. The major significance of the higher pressure is the improved denitrification, with small changes in overall yields. The denitrification activity after 1400 hours operation of the catalyst at the higher pressure is better than the start of run activity at the lower pressure.

Based on the pilot plant yields, we predict a 65 volume per cent yield of 650°F minus liquid product in the refining of the Paraho shale oil at Toledo. The average chemical hydrogen consumption should be in the range of 1600-1700 SCFB (standard cubic feet per barrel). Actual hydrogen consumption will be higher due to dilution and bleed losses. The nitrogen levels in the jet fuels before acid treating will be in the range of 2000-3000 ppm, and in the DFM in the range of 4000-5000 ppm.

To determine what boiling ranges would be required to meet product specifications, part of the 650°F minus liquid was cut into 25°F boiling range fractions. These fractions were then blended to make JP-4, JP-8, JP-5 and DFM. The key specifications used to determine these blends were freeze and flash points on the jet fuels, and pour and cloud points on the DFM. It was determined that the cutpoints for the various products would be:

<u>Product</u>	<u>Boiling Range</u>	<u>Key Specifications</u>
JP-4	C ₅ - 460°F	-72°F Freeze Point
JP-8	335° - 460°F	105-130°F Flash Point, -58 Freeze Point
JP-5	360° - 480°F	140°F Flash Point, -51°F Freeze Point
DFM	480° - 650°F	30°F Cloud Point, 20°F Pour Point

The remainder of the 650°F minus product was fractionated to make the desired quantities of the above products for subsequent treating. The 650°F plus material was used to make the heavy fuel requirements. The gasoline stocks were made from the C₅ - 335°F and C₅ - 360°F material produced when making the JP-8 and JP-5 stocks.

The predicted yields from the 650°F minus liquid product are:

	<u>Volume % of</u> <u>650°F Minus</u>	<u>Volume % on</u> <u>Shale Oil</u>
Gasoline Stocks	9%	6%
JP-5	37%	24%
DFM	54%	35%

The actual yield of the JP-5 will be less than the 24 volume per cent on shale oil, since the JP-4 and JP-8 also contain some of the same boiling range material. Yields of all products will be affected by the mechanical limitations of the Toledo fractionation equipment.

To improve the stability of the jet and diesel fuels, these stocks were treated with sulfuric acid, filtered, and clay treated. The acid treat levels varied depending upon the nitrogen content of the fuel being treated. With acid treating, the nitrogen content of some JP-5 samples were reduced from ~2500 ppm to less than 10 ppm. Acid treated JP-5 easily passes the JEFTOT stability test. After acid treating, the stability specifications can be met on both the jet fuels and DFM products. The liquid yields from acid treating will be in the range of 90 to 95%, depending on feed nitrogen levels.

The predicted products yields from the refining of 100,000 barrels of Paraho shale oil at Sohio's Toledo Refinery are:

JP-4	2500 barrels
JP-8	500 barrels
JP-5	18500 barrels
DFM	29000 barrels

The JP-4 and JP-8 volumes have been specified by the Navy. After these quantities have been produced, the emphasis is to maximize JP-5 and DFM yields. The yields are predictions after projected losses for acid and clay treating. Actual yields may be reduced due to fractionation equipment limitations.

The major problem encountered in the pilot plant operation was the formation of an iron-arsenide deposit in the preheat section. Originally, Sohio had planned to sacrifice the top portion of the catalyst bed and not try to remove the arsenic compounds before the reactor. However the iron-arsenide deposit required that an alumina guard bed be installed in front of the preheat section to prevent pluggage.

Refining Plan

The refining of the Paraho shale at Sohio's Toledo Refinery is scheduled for this fall. The shale oil will be shipped by railcar from Anvil Points, Colorado to Toledo, Ohio. The shipping and receiving of the shale oil will take two to three months.

The shale oil unloading facilities and storage tank will be segregated from the normal refinery operations to prevent contamination. Also, new product rundown lines will be installed from Hydrocracker I to the product storage tanks. All existing tankage used for the run will be cleaned before use. During the run, the Hydrocracker, acid treater, and clay treater will be isolated from the normal refinery operation.

Before feeding the shale oil to the Hydrocracker unit, it will be heated to $\sim 175^{\circ}\text{F}$ to facilitate water and solids settling. It will then be fed to the Hydrocracker reaction section. A portion of the 650°F plus material will be combined with the fresh feed to improve jet and diesel fuel yields.

From the reaction section, the treated shale oil will be hydrogen stripped and fed to the Splitter Tower. The Splitter Tower will fractionate the treated shale oil into four cuts:

1. Gasoline Stock
2. Jet Fuel Cut
3. DFM
4. Bottoms

For most of the 30-day run, the Splitter Tower conditions will be set to make JP-5 from the jet fuel cut. However, the

conditions will be adjusted to produce ~500 barrels of JP-8 and ~2500 barrels of JP-4.

The jet fuel will be acid and clay treated on rundown. The JP-8 and JP-4 products will be loaded directly onto railcars for product shipment. The JP-5 will be stored in the refinery and shipped after the run is completed. The DFM will be run-down directly to tankage. It will be acid and clay treated after the run. Any heavy fuel the Navy wishes to take as product will be loaded directly on rundown. The remainder will be disposed of in the refinery.

Conclusions

Based on the Phase I pilot plant work the following conclusions were reached:

1. A guard bed will be required for the refining run.
2. Military specification fuels can be produced from Paraho shale oil with the combination of hydroprocessing and acid-clay treating.
3. Toledo's Hydrocracker I hydrogen partial pressure should be adequate for the demonstration run.

4. Expected product yields at Toledo are:

JP-4*	2500 barrels
JP-8*	500 barrels
JP-5	18500 barrels
DFM	29000 barrels

* Fixed volume requested

5. Actual product yields may be less due to fractionation equipment limitations.
6. Additional areas for future work should be:
 - a. Shale oil pretreatment
 - b. Optimizing hydroprocessing conditions
 - c. Product stability.

FIGURE I
COKING AS FIRST STEP

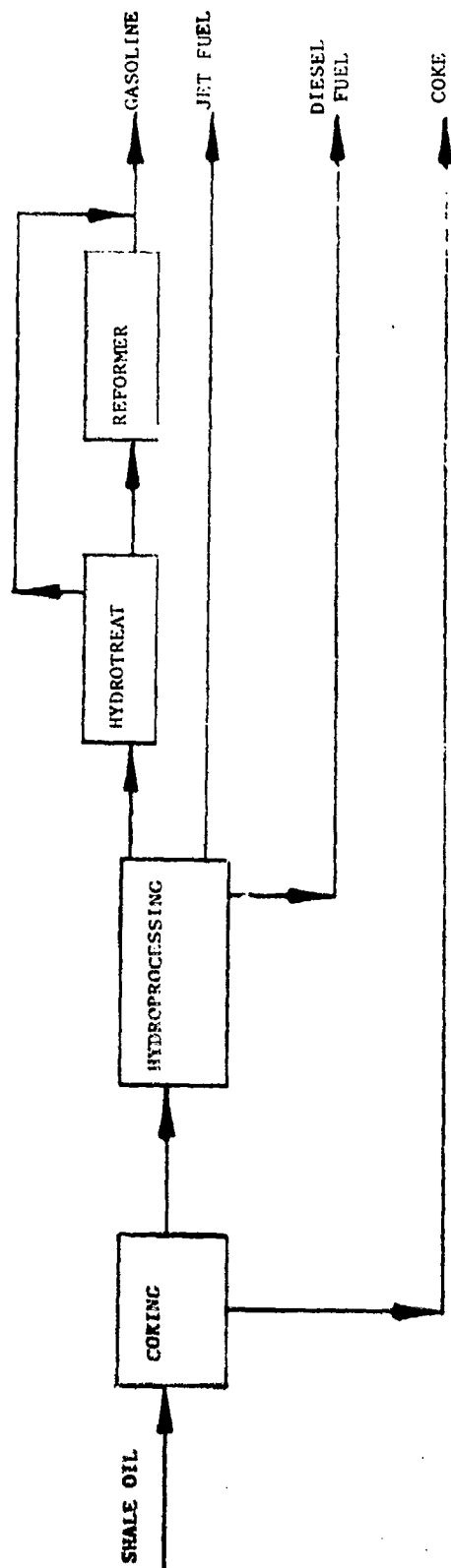


FIGURE II.
CRUDE UNIT AS FIRST STEP

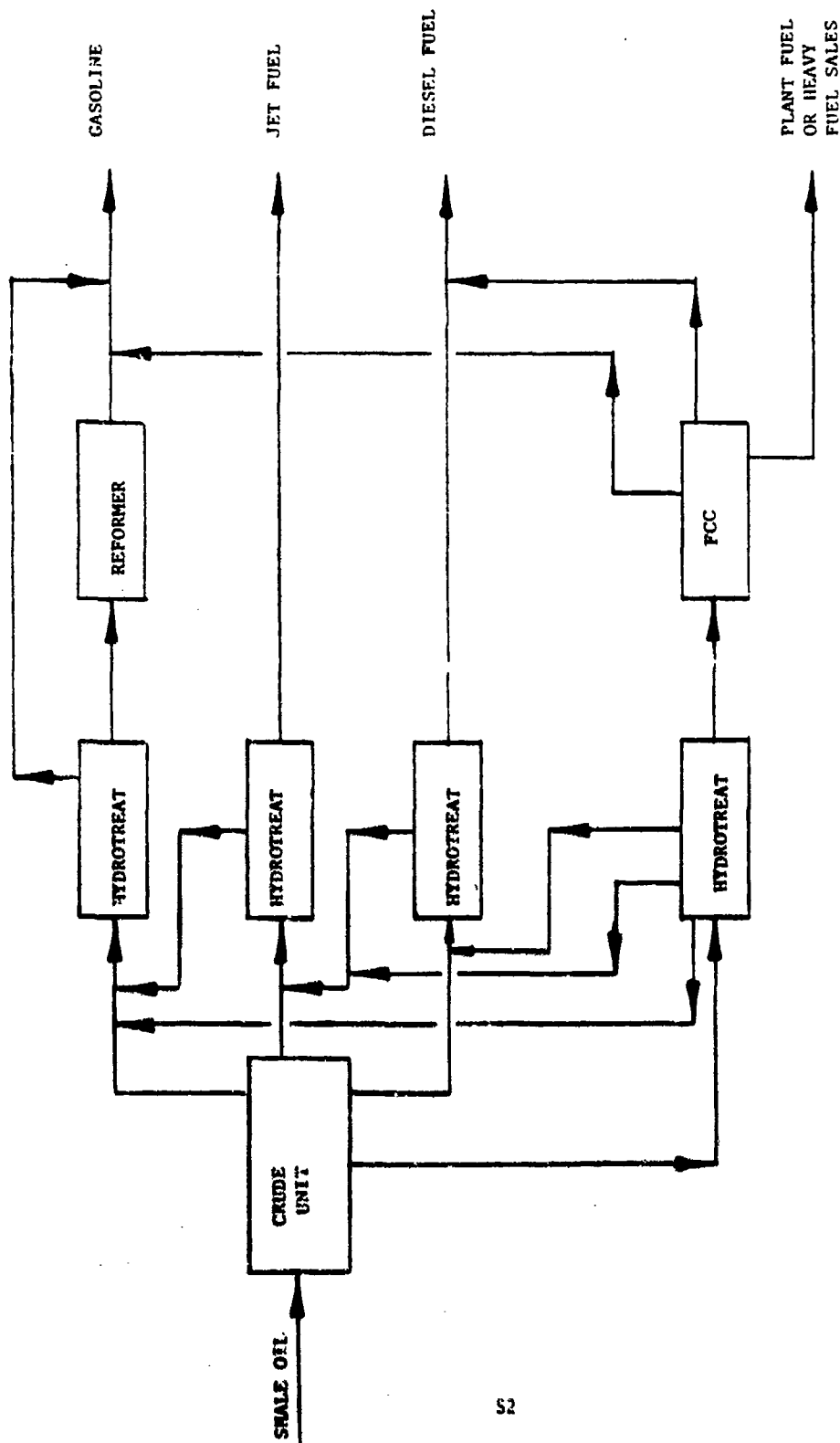


FIGURE 111

HYDROPROCESSING AS FIRST STEP

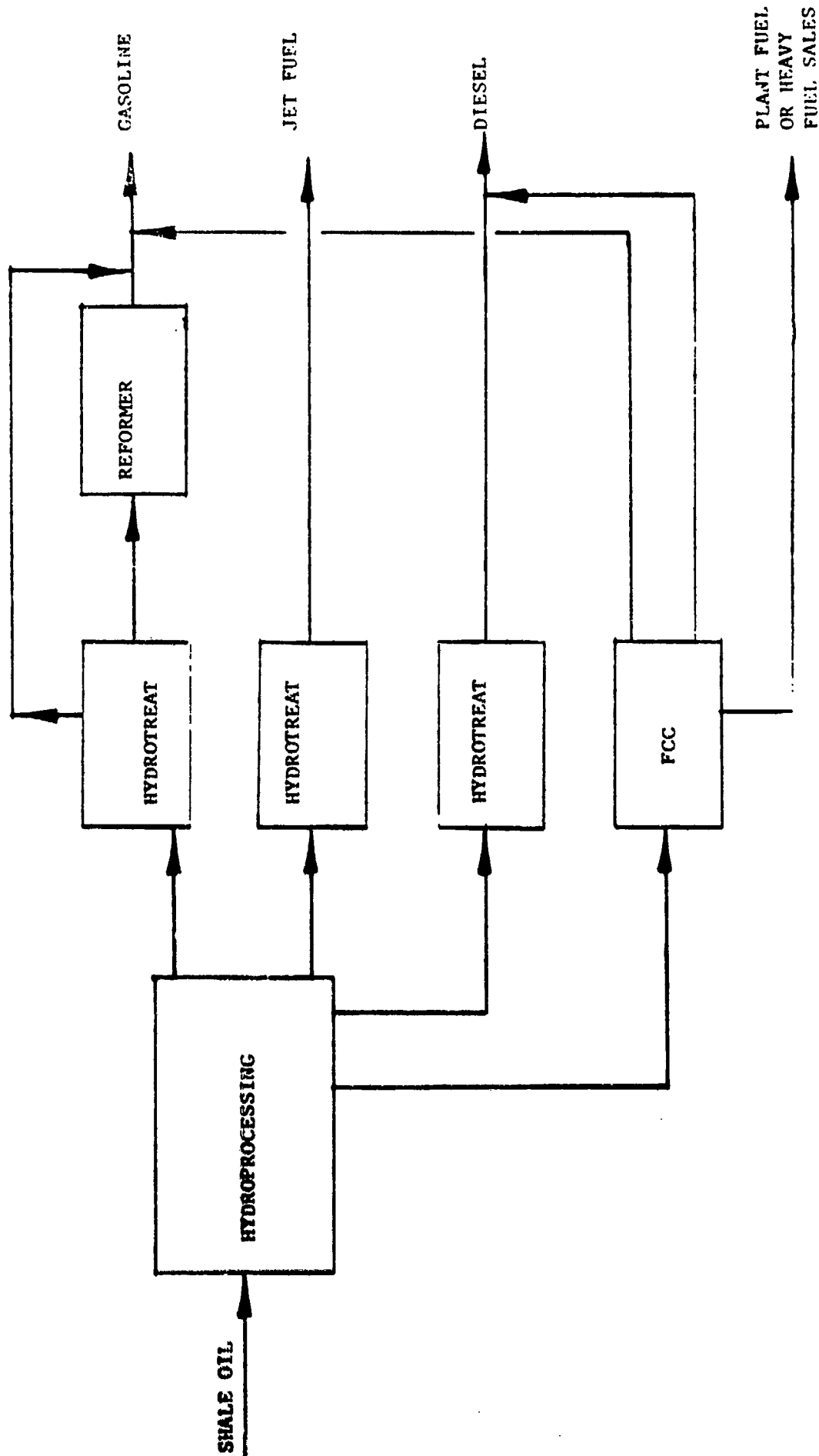


FIGURE IV

TOLEDO BLOCK FLOW

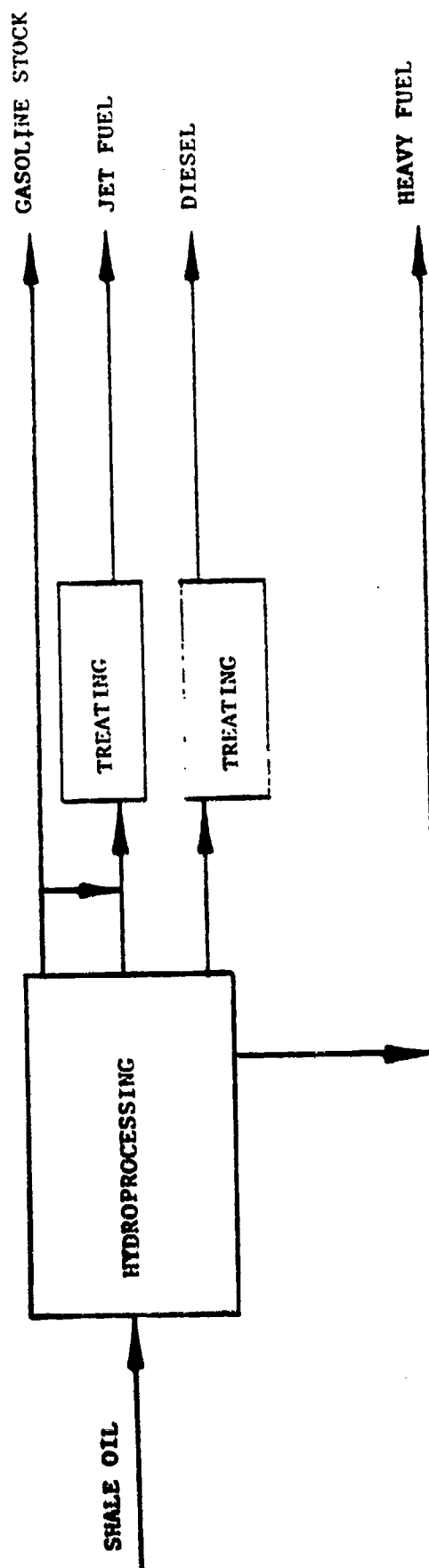


TABLE I - BASE YIELDS

	SOR				EOR			
	<u>WT %</u>	<u>°API</u>	<u>VOL %</u>	<u>WT% N</u>	<u>WT %</u>	<u>°API</u>	<u>VOL %</u>	<u>WT% N</u>
H ₂	- 2.6				- 2.5			
NH ₃ /H ₂ S/H ₂ O	4.0				3.3			
C1	1.0				1.2			
C2	1.0				1.5			
C3	0.9				1.1			
C4	0.9	111.0	1.5		1.1	111.0	1.8	
C5	1.0	92.7	1.6		1.1	92.7	1.8	
C6-315°F	6.3	58.0	7.9	0.05	4.8	56.2	6.0	0.08
315-480°F	22.2	42.2	25.3	0.25	21.8	41.9	24.9	0.40
480-650°F	31.9	33.3	34.5	0.43	33.5	33.3	36.4	0.76
650+ Btms.	33.4	28.7	35.2	0.22	33.1	27.5	34.7	0.59

**Component Analysis of Paraho Shale Oil
and Hydrotreated Products**

	<u>Paraho Shale Oil Feedstock</u>	<u>Mid Run Hydrotreater Products</u>	
		<u>650 °F Minus</u>	<u>650 °F Plus</u>
Hydrogen, wt%	11.32	13.04	12.83
Carbon, wt%	84.71	85.84	86.09
Nitrogen, wt%	2.13	0.32	0.27
Oxygen, wt%	1.35	0.67	0.28
Sulfur, wt%	0.68	*	*
Metals, ppm			
As	9.6	N11	N11
V	0.2	N11	N11
Fe	38.0	N11	N11
Ni	1.9	N11	N11
°API	20.3	37.8	28.7
Mole Weight	297	218	336
Ash	0.011	-	-
BS&W	0.1	-	1.6
Carbon Residue, wt%	0.842	-	-
Asphaltenes, wt%	1.099	-	0.185
Aniline Point, °F	137	146.5	217
Pour Point, °F	-	10	110
Distillation	D-1160	D-86	D-1160
IBP	376	IBP 262	IBP 718
5	464	10 369	5 767
30	655	50 526	30 799
50	791	90 642	50 827
70	878	EP 670	70 964
90	1015	Residue 1%	90 982
Residue	10%	Loss 0%	Residue 7%
Loss	0%		Loss 0%

* Sulfur on hydrotreated products was less than 20 ppm

TABLE II - YIELDS AT INCREASED PRESSURE

	<u>WT %</u>	<u>°API</u>	<u>VOL %</u>	<u>WT% N</u>
H ₂	- 2.8			
NH ₃ /H ₂ S/H ₂ O	4.2			
C1	1.4			
C2	1.1			
C3	0.7			
C4	1.2	111.0		
C5	2.2	92.7		
C6-315°F	4.6	56.2	5.7	0.02
315-480°F	19.9	43.0	22.9	0.11
480-650°F	30.2	33.9	32.9	0.23
650+ Btms.	37.3	29.0	39.9	0.18

JET FUELS - THE REFINER'S OUTLOOK

by: W. G. Dukek

Exxon Research and Engineering Company

Liquid hydrocarbon fuels for aviation will continue to be made primarily from petroleum for the remainder of this century; synthetics will provide only 2% of the demand for oil products by 1990 (Fig. 1 and 2). In this time period, imported crude will still be necessary to supply about half of the U.S. oil demand. Aviation fuels are part of the fast growing family of distillates which are outpacing the demand for gasoline and will require changes in refinery processing to make a different slate of products in the future (Fig. 3, 4 and 5).

At present, refiners are required to manufacture about twice as much gasoline as distillate and utilize catalytic cracking of heavy gas oil to upgrade fuel oil fractions to these lighter products (Fig. 6). However, aviation fuels are usually virgin cuts from the pipestill and must compete with the other uses of these fractions in blending diesel fuel and burner fuels. Currently cheap hydrogen is available from catalytic reforming units to desulfurize and treat distillate and aviation blending stock.

Jet A kerosene for commercial airlines is the primary aviation fuel and requires about 6% of the crude barrel today, a fraction expected to grow to 9% in 10 years (Fig. 7). JP-5, the kerosene fuel evolved to serve naval aviation, presents refiners with a difficult challenge because of its narrowly defined distillation range; the high flash point required for safety in shipboard handling and the low freezing point required for extended aircraft missions limits the potential output to about 3% of crude (Fig. 8).

Refiners are faced with an increasing supply of marginal crudes to meet the challenge posed by aviation fuels with their critical quality requirements of low sulfur content and aromatics limitations. For example, growing imports of Arabian crude require more desulfurization capacity and corrosion protection of refineries designed for sweet domestic crudes. The present but temporary glut of North Slope crude in excess of West Coast refining capacity illustrates the imbalance in processing capability that can develop when a marginal crude must be handled. The impact of these crudes on aviation fuel can be seen by the growing aromatic levels of Jet A fuel, a factor which has made specification relaxations necessary (Fig. 9).

The refinery of the future, faced with a different gasoline vs. distillate demand closer to 1:1 compared with 2:1 today will utilize conversion processes such as hydrocracking of heavy gas oil to maximize distillate output (Fig. 10). This process sequence will require expensive manufactured hydrogen and result in a much more energy-intensive refinery. The aviation fuels that will be blended to meet future demand will be even higher in aromatics level than today's Jet A, particularly if a higher freezing point diesel type fuel becomes acceptable for domestic airline use (Fig. 11).

Future JP-5 will be even more difficult to manufacture especially if additional hydrogenation is needed to lower aromatics or to reduce nitrogen levels (Fig. 12). To increase yields of this high flash point kerosene, refiners may need to improve fractionation efficiency or rerun the pipestill product. Process steps like hydrogenation carry the penalty of potential lubricity and peroxidation problems in aircraft fuel systems and additives to cope with these problems will be as necessary as ever. However the petroleum industry can be expected to meet the Navy's aviation fuel needs for the foreseeable future (Fig. 13 and 14).

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2. U.S. Oil Supply
3. U.S. Domestic Demand for Motor Gasoline
4. Domestic Distillate Demand
5. U.S. Demand for Jet Fuels and No. 1 F.O.
6. Product Yield vs. Demand
7. Distillation Range of Liquid Fuels
8. Jet Fuel Yields
9. Average Aromatic Content
10. Maximizing Distillates in Future Refinery
11. Blending Distillates in a 1990 Refinery
12. Energy Consumed in Refining Marginal Jet Fuels
13. Future JP-5 Quality Problems
14. Summary of Fuel Refiner's Outlook

JET FUELS - THE REFINER'S OUTLOOK

- PETROLEUM AS PRIMARY SOURCE OF LIQUID FUELS
- IMPORTS OF 50% STILL NEEDED
- DISTILLATE DEMAND OUTPACING GASOLINE DEMAND
- JP-5 VS. OTHER AVIATION FUELS
- CONVERSION PROCESSES FOR DISTILLATES
- FUTURE AVIATION PRODUCT QUALITY

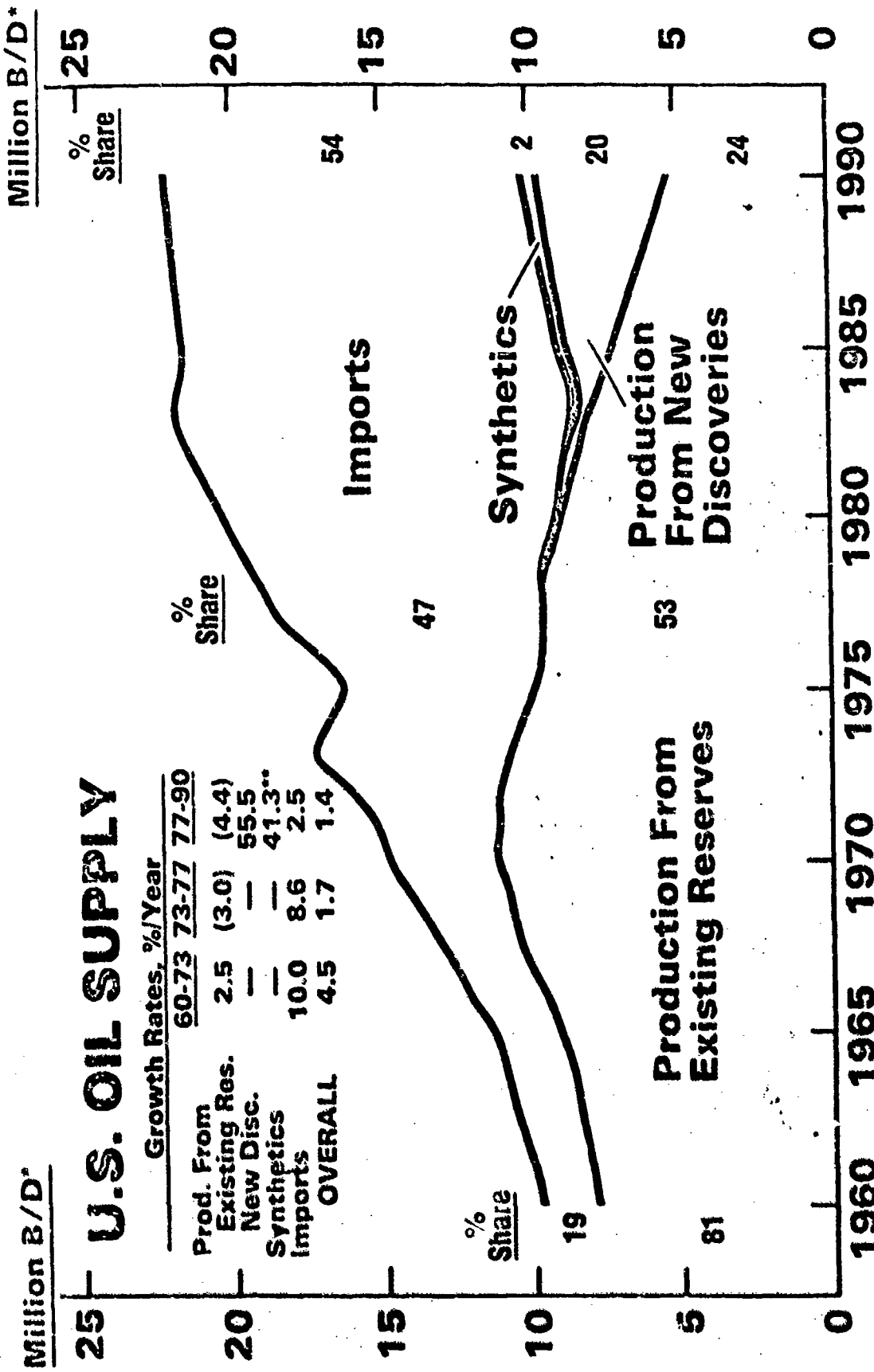
FIG. 1

Million B/D*

U.S. OIL SUPPLY

Growth Rates, %/Year

	60-73	73-77	77-90
Prod. From Existing Res.	2.5	(3.0)	(4.4)
New Disc.	—	—	55.5
Synthetics	—	—	41.3**
Imports	10.0	8.6	2.5
OVERALL	4.5	1.7	1.4



*Million Barrels/Day **For 1983-1990 only

FIG. 2

United States Domestic Demand For Motor Gasoline

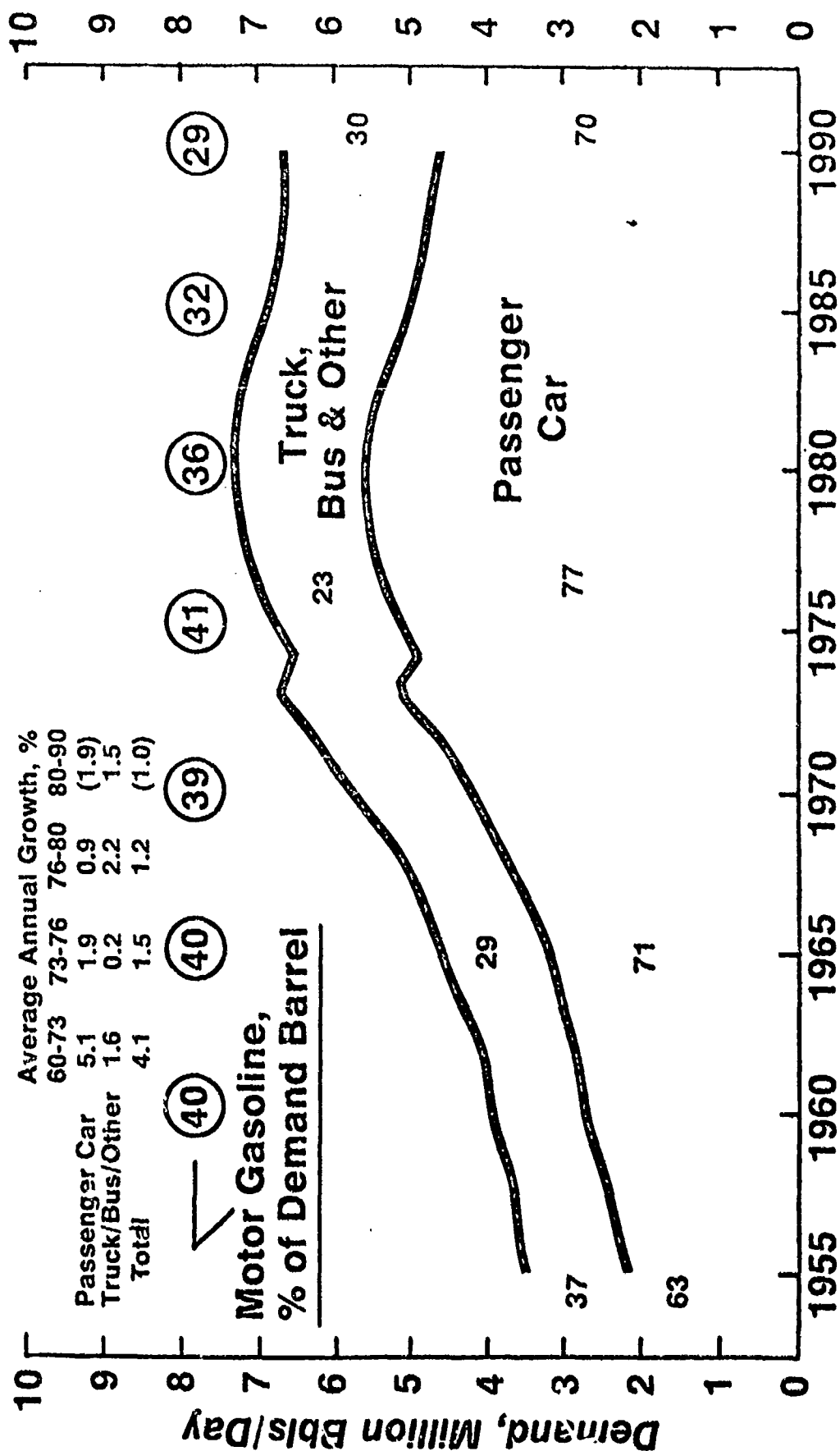


FIG. 3

Domestic Distillate Demand, MB/D

End-use Demand Changes

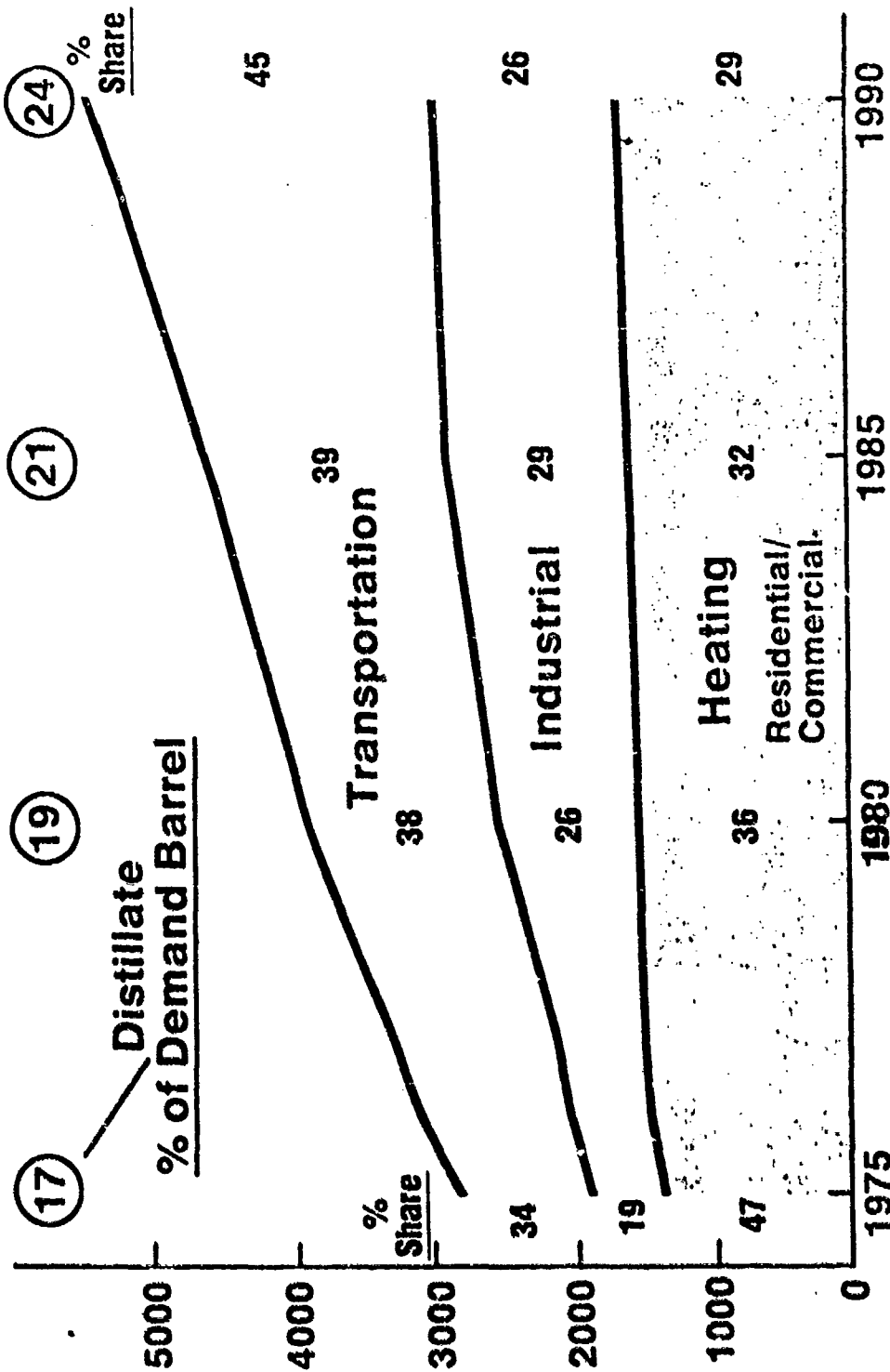


FIG. 4

U.S. DEMAND FOR JET FUELS AND No. 1 F.O.

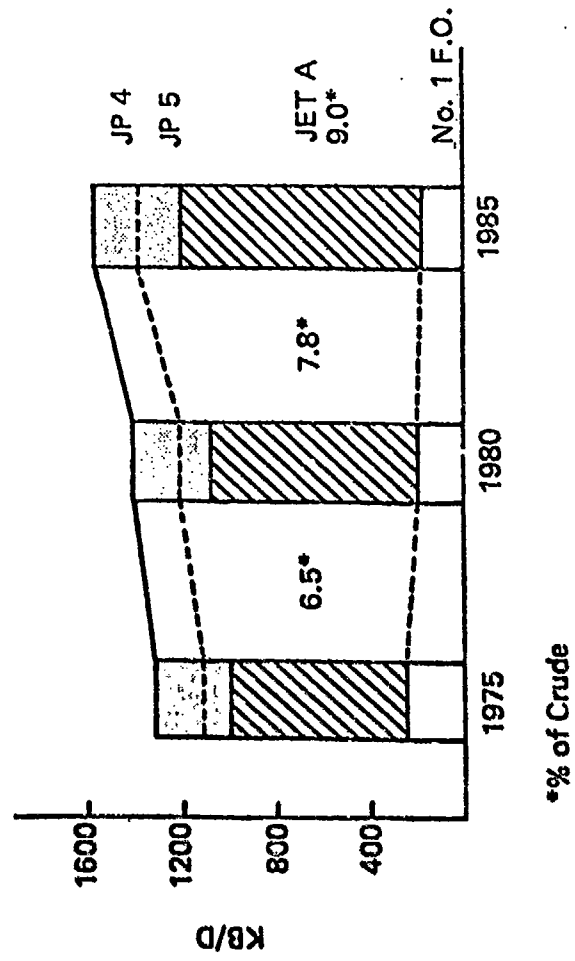


FIG. 5

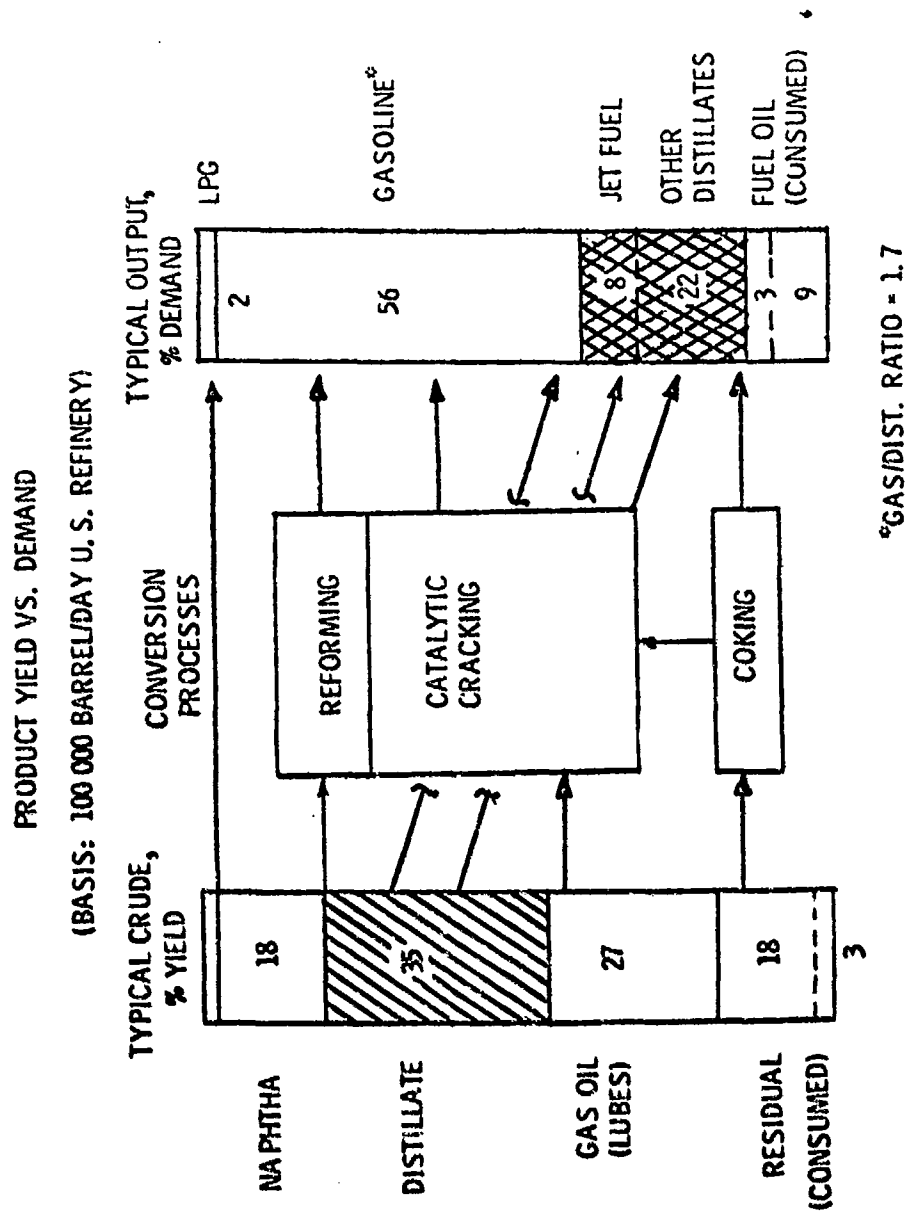


FIG. 6

DISTILLATION RANGES OF LIQUID FUELS

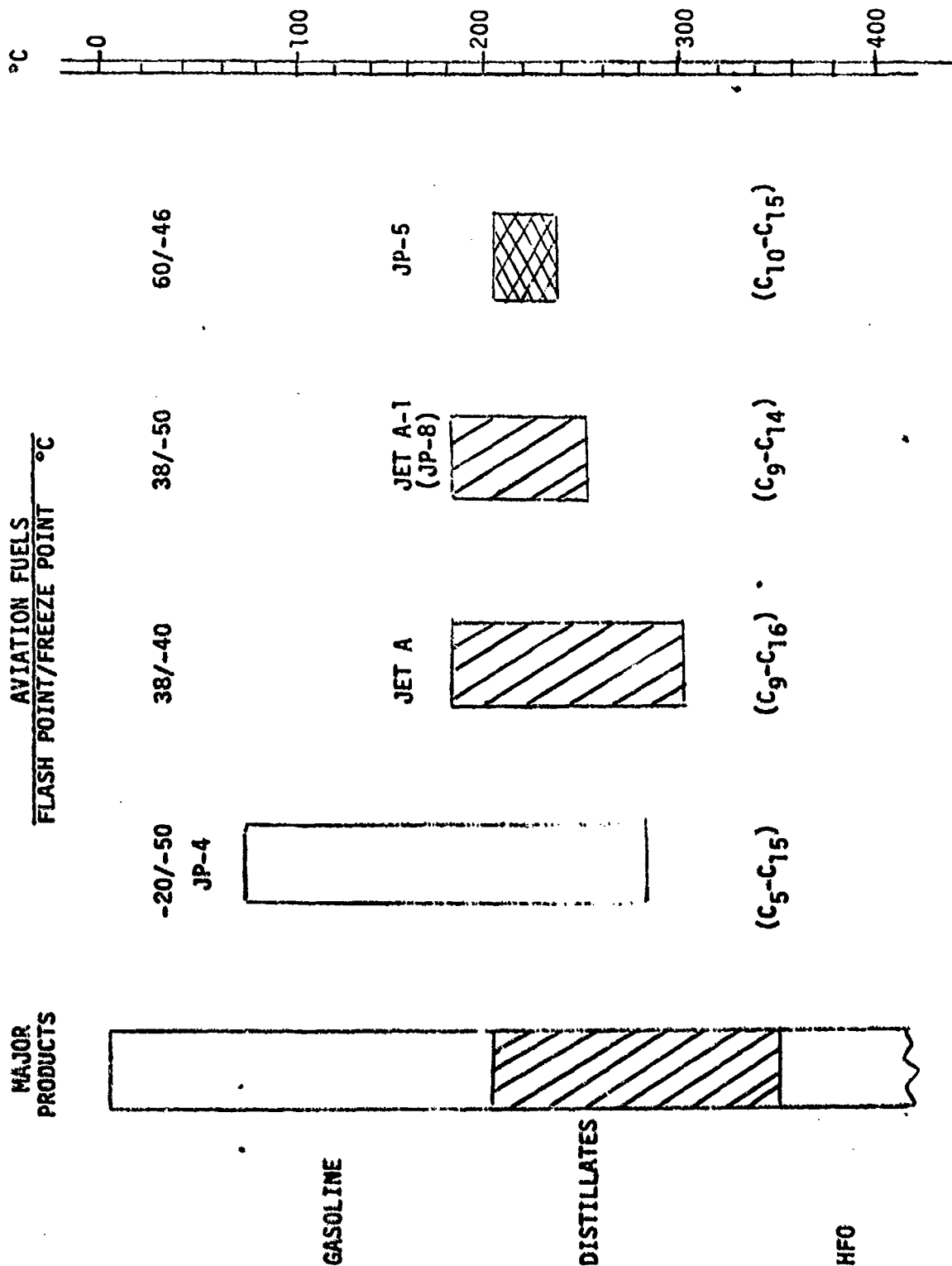


FIG. 7

JET FUEL YIELDS FROM TYPICAL REFINERIES

FUEL GRADE	FLASH POINT / °C	VOL. % YIELD*			PRACT MAXIM
		REFINERY A	REFINERY B	REFINERY C	
JET A	38/-40	19.6	27.0	17.0	12
JET A-1	38/-50	13.6	18.5	11.5	6
JP-5	60/-46	5.2	12.4	5.1	3

* THEORETICAL YIELDS FROM ASTM FLASH POINT SYMPOSIUM PAPER, DECEMBER 1977

REFINERY A: EUROPEAN REFINERY USING MIDDLE EAST CRUDES

REFINERY B: U.S. GULF REFINERY - MIXED DOMESTIC/IMPORTED CRUDES

REFINERY C: U.S. REFINERY - ALASKAN NORTH SLOPE CRUDES

FIG. 8

AVERAGE AROMATIC CONTENT OF U.S. JET A FUEL - ACTUAL AND PROJECTED

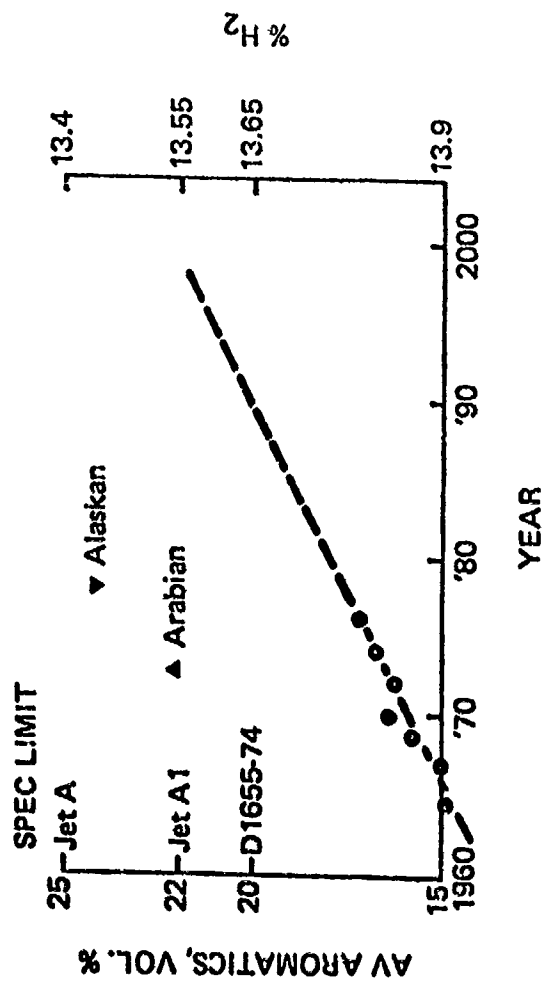


FIG. 9

MAXIMIZING DISTILLATES IN A 1990 TYPE REFINERY

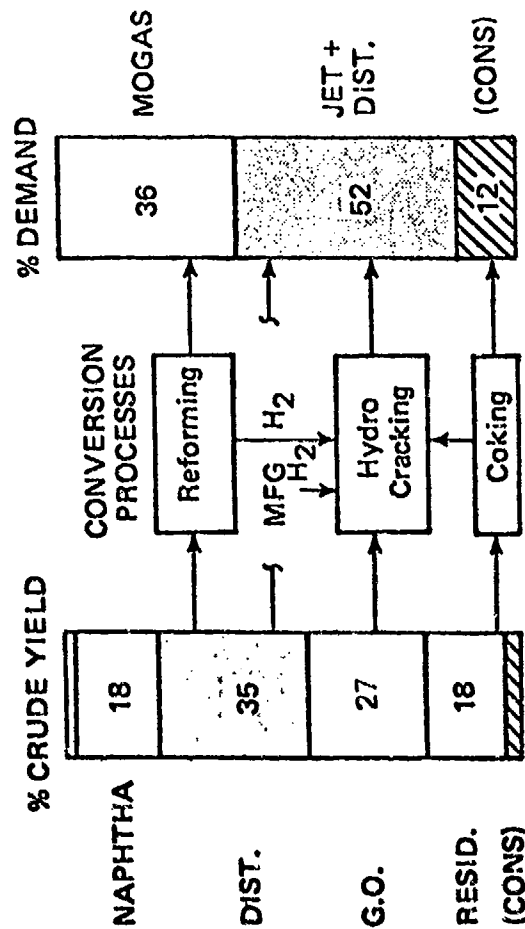


FIG. 10

BLENDING DISTILLATES IN A 1990 TYPE REFINERY

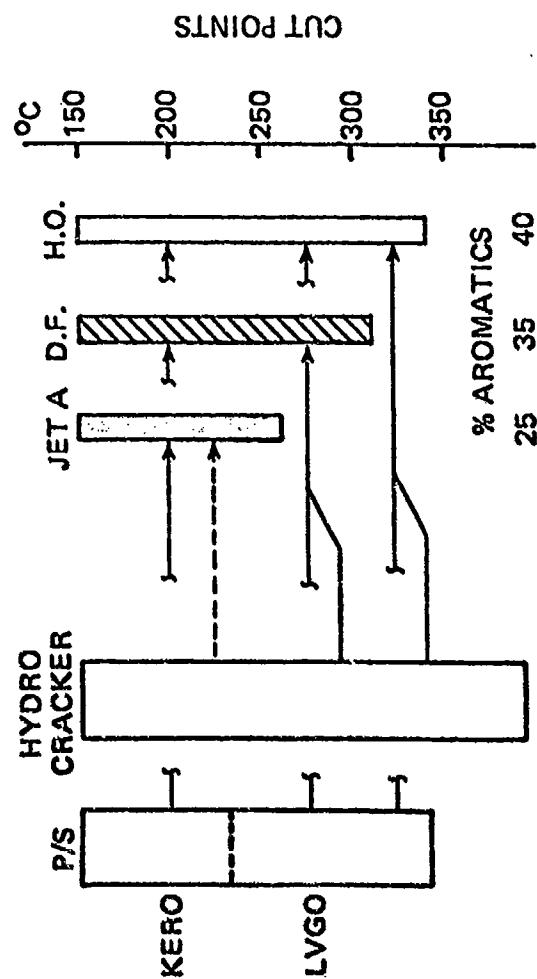


FIG. 11

**ENERGY CONSUMED IN REFINING
MARGINAL JET FUELS**

<u>PRIORITY</u>	<u>CUT</u>	<u>CRITICAL PROPERTY</u>	<u>% ENERGY REQUIRED</u>
1.	P/S DISTILLATE	AROMATICS	3
2.	HVY VIRGIN NAPHTHA	FREEZE POINT FLASH POINT	3
3.	HYDROFINED CAT DISTILLATE	AROMATICS VISCOSITY	6
4.	HYDROCRACKATE	AROMATICS VISCOSITY	12
5.	HYDROGENATED HYDRO- CRACKATE	VISCOSITY	20
6.	HYDROTREATED SYNTHETICS	AROMATICS VISCOSITY	20-30

FIG. 12

FUTURE JP-5 QUALITY PROBLEMS

<u>CRITICAL QUALITY</u>	<u>PROCESSING REQUIRED</u>	<u>POTENTIAL FUEL SYSTEM EFFECTS</u>	<u>REMARKS</u>
SULFUR (MERCAPTAN)	HYDROFINING		
AROMATICS (H ₂ CONTENT)	HYDROGENATION	LUBRICITY	ADDITIVE REQUIRED
STABILITY (NITROGEN ?)	HYDROGENATION	PEROXIDATION	ANTIOXIDANT REQUIRED
VOLATILITY (FLASH POINT)	RERUNNING	FLAMMABILITY	LIGHT ENDS CONTROL
VISCOSITY	RERUNNING	ATOMIZATION	HEAVY ENDS CONTROL

SUMMARY OF JET FUEL REFINER'S OUTLOOK

- DEPENDENT ON IMPORTED AND MARGINAL CRUDE
- SYNTHETICS WILL BE MINOR SOURCE TILL 2000
- U.S. REFINERS MUST MAXIMIZE DISTILLATES
- CONVERSION REFINERIES ARE ENERGY INTENSIVE
- AVIATION COMPETES WITH OTHER DISTILLATE USERS FOR KEROSENE
- JET FUELS WILL INCREASE IN AROMATICS
- JP-5 WILL CONTINUE TO BE DIFFICULT TO MAKE

FIG. 14

REFINING STUDIES ON SHALE OIL

by: R. F. Sullivan

Chevron Research Company

Chevron Research Company conducted extensive laboratory, pilot plant, and engineering studies to demonstrate the feasibility and estimate costs for refining of surface-retorted Paraho shale oil. These studies showed that raw shale oil can be conventionally refined using advanced, commercialized petroleum technology to produce finished transportation fuels, primarily motor gasoline, kerosene jet fuel, and diesel fuel.

Three alternative refining routes were evaluated: (1) hydrotreating followed by hydrocracking, (2) hydrotreating followed by fluid catalytic cracking, and (3) coking followed by hydrotreating. In addition, a fourth alternative was evaluated where raw shale oil was hydrotreated to produce a synthetic crude suitable for processing in an existing refinery.

Shale oil is sufficiently different from most petroleum crudes that refining presents unusual problems. The shale oil used in this study contained over 2 wt % nitrogen compared to less than 0.3% for most petroleum crudes. It also contained sulfur, arsenic, and oxygenated,

Encl. - Figure 1 (RE 781767)
Figure 2 (RE 781764)
Figure 3 (RD 780518-1)
Figure 4 (RE 781765)
Figure 5 (RE 782382)
Figure 6 (RE 782292)
Figure 7 (RE 781762)
Figure 8 (RE 781761)
Figure 9 (RE 781763)
Figure 10 (RE 781760)
Figure 11 (RE 781759)
Figure 12 (RE 782297)

¹Adapted from Technical Summary of DOE Interim Report, "Refining and Upgrading of Synfuels from Coal and Oil Shales by Advanced Catalytic Processes: Processing of Paraho Shale Oil," by R. F. Sullivan, D. E. Stangeland, C. E. Rudy, D. C. Green, and H. A. Frankin, FE 2315-25, Dist. Category UC-90d, published April 1978. (Available from the Division of Oil, Gas, and Shale Technology, U.S. Department of Energy, 400 First Street, Railway Labor Building, Washington, D.C. 20545.)

unsaturated, and metallic contaminants or impurities (Figure 1). These prevent its being mixed with crude oils for normal refinery processing.

The key to successful refining of whole shale oil is an effective initial hydrotreating process. This removes the contaminants and permits subsequent conversion to proceed through established hydrocracking or fluid catalytic cracking units. Distillates from coking of raw shale oil also require subsequent hydrotreating to remove residual impurities and meet final product specifications.

Pilot plant tests showed that the nitrogen in shale oil can be reduced to levels as low as 1 ppm in a single processing step (Figure 2). However, evaluation of the results indicated that it is adequate and economically advantageous to hydrotreat to an intermediate nitrogen level of about 500-1500 ppm in the whole liquid product. This product can be refined to high quality transportation fuels using conventional refining technology. (Figure 3 is a schematic flow diagram showing the various processing steps in the pilot plant studies.)

The key hydrotreating step was demonstrated in a 3500-hour pilot plant test in which whole shale oil was hydroprocessed to about 500 ppm product nitrogen over Chevron ICR 106 catalyst (Figures 4 and 5). Products from the hydrotreated shale oil are primarily (1) a 650°F+ gas oil that is similar in most respects to normal gas oil feeds to hydrocrackers and fluid catalytic cracking units (Figure 6), (2) a middle distillate fraction that can be converted to salable diesel and jet fuel by additional hydrotreatment (Figures 7 and 8), and (3) naphtha that is a suitable feed to a two-stage catalytic reformer.

If hydrocracking is the major conversion process after hydrotreating, pilot plant studies show that the gas oil fraction can be converted to a stable, low nitrogen, high smoke point jet fuel plus additional naphtha for reforming to high octane gasoline (Figures 9 and 10). Alternatively, hydrocracking conditions could be adjusted to produce primarily either gasoline or diesel fuel. If fluid catalytic cracking is the major conversion process, the main products are high octane gasoline and light cycle oil that can be further hydrotreated to diesel fuel. In the coking alternative, raw shale oil is fed directly to the coker; and the distillate product is hydrotreated to diesel fuel and a naphtha suitable for catalytic reforming to motor gasoline (Figure 11).

The overall yields of finished transportation fuels for the cases studied ranged between 78 vol % of shale oil feed for the coking case to 91-95 vol % for the hydrocracking and fluid catalytic cracking cases, respectively. These yields represent the net amount of light products after subtracting refinery fuel and hydrogen plant feed, which were internally supplied. The net yields of transportation fuels for each case are as follows:

Major Conversion Process	Hydrocracking	Fluid Catalytic Cracking	Coking
Product Type, LV % Net Yield from Dewatered Raw Shale Oil Feed			
Propane-Butane (LPG)	0	0	2
Motor Gasoline	17	38	17
Kerosene Jet Fuel	20	0	0
Diesel Fuel	<u>54</u>	<u>57</u>	<u>59</u>
Total Transportation Fuel	91	95	78

Product yields can be varied depending on demand. For example, in the hydrocracking case, the quantity of kerosene jet fuel could be increased to perhaps 50-60% of the total product plus additional naphtha. If military jet fuel such as JP-4 is also a target product, it would include much of the naphtha, giving an even higher yield of total jet fuel. Additional pilot plant and engineering studies would be required to more clearly define the processing conditions and costs for these cases.

Screening-type process designs and estimated refining costs were developed for each of the three process routes listed above based on producing (1) 50,000 BPCD of transportation products from a "grass roots" refinery in a remote Rocky Mountain location and (2) 100,000 BPCD of transportation products from a "grass roots" refinery located near a Rocky Mountain or Mid-Continent urban center. The costs for hydroprocessing to produce a synthetic crude were estimated both for a "grass roots" site near the shale oil retorting facilities and for location at a typical existing Mid-Continent refinery. All refineries were designed with facilities to meet present environmental requirements and anticipated near-term environmental and energy conservation regulations.

Results of the cost studies showed that refining of crude Paraho shale oil to finished transportation fuels in new "grass roots" facilities would cost about \$8-\$10 per barrel for 100,000 BPCD and about \$10-\$12 per barrel for 50,000 BPCD of light products at today's (First Quarter 1978) costs. Figure 12 summarizes the costs for the 100,000 BPCD cases. Refining to a synthetic crude would cost about \$6.50 per barrel, not including costs for downstream processing. The synthetic crude would be suitable for further upgrading into finished products in a large percentage of existing refineries.

As outlined above, the hydrocracking and fluid catalytic cracking cases show a much higher yield of light products from raw shale oil than the coking case, which is the lowest cost plan. The fluid catalytic cracking case has a slight advantage in cost and yield over hydrocracking, but the latter provides greater flexibility for varying individual product yields. Hydrocracking is the only scheme capable of efficiently maximizing jet fuel production.

The total processing costs given above include capital charges based on a 15% discounted cash flow (DCF) rate of return on investment. In the report, total processing costs are presented covering DCF rates of return in the range of 10% to 20%. For evaluating new projects, a 15% DCF rate of return is often used in industry as a checkpoint below which the justification for investment becomes increasingly questionable. Taking into account that the production of oil from shale is an unproven venture with significant internal and external uncertainties and risks, the appropriate rate of return to be used in economic analysis of this new technology should be at least this high.

In order to obtain the total cost of producing finished light products from shale, it would be necessary to add to the above processing costs, the cost of resource acquisition, shale mining, handling, retorting, and waste disposal, and the transportation of raw shale oil. In the case of hydroprocessed synthetic crude, the downstream refining costs to produce finished products also need to be included.

Areas for future study also were identified. None of these appears to represent a major problem. Rather, most involve second-order process refinements that will be incorporated in future commercial projects which are based on specific product slates.

FIGURE 1
PROPERTIES OF
DEWATERED PARAHO SHALE OIL

Gravity, °API	20.2
Sulfur, Wt %	0.66
Total Nitrogen, Wt %	2.18
Oxygen, Wt %	1.16
Arsenic, ppm	28
Iron, ppm	70
Ash, Wt %	0.03
Pour Point, °F	90
Ramsbottom Carbon	1.85
TBP Distillation, %	°F
Start	183
10	453
50	736
70	842
95	1053

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FIGURE 2

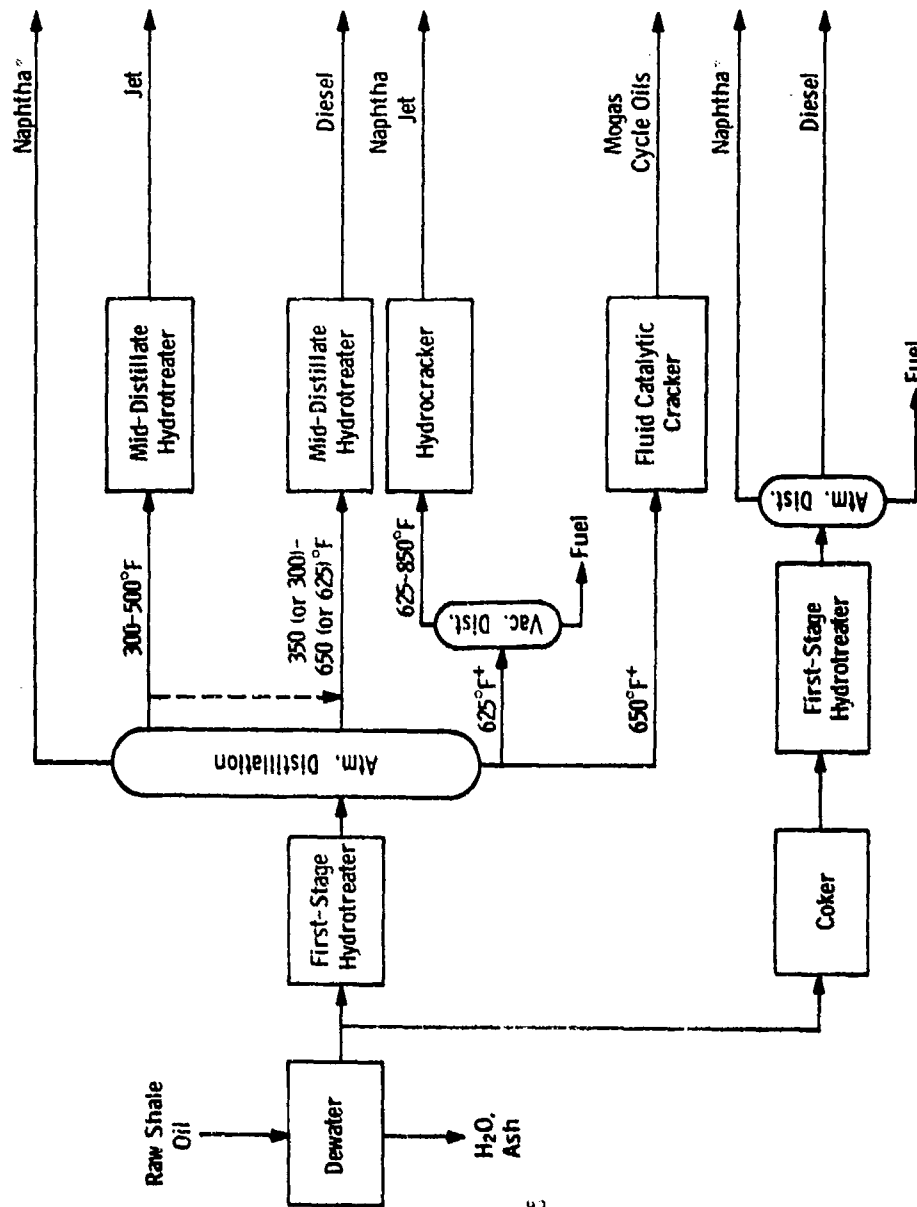
EFFECT OF PRODUCT NITROGEN ON
HYDROTREATED WHOLE SHALE OIL PROPERTIES

Catalyst: ICR 106 (Ni - W - SiO₂ - Al₂O₃)
Conditions: H₂ Pressure, psia - 1850
Catalyst Temp., °F - 742-767
LHSV - 0.2-0.6

	Feed	Product			
	21,800	2,800	505	30	1.3
Nitrogen, ppm					
Inspections					
Gravity, °API	20	34	36	38	40
Sulfur, ppm	6,600	145	45		
Pour Point, °F	90	80	85	80	
Ramsbottom Carbon, Wt %	1.85		0.08	0.06	0.02
Group Type, LV %					
Paraffins		34	33	35	36
Naphthenes		37	46	48	53
Aromatics		29	21	17	11
95% Point by TBP Distillation, °F	1,053	958	938	906	855

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FIGURE 3
PILOT PLANT TESTS FOR PROCESSING SHALE OIL



* Naphtha to be Converted to High Octane Gasoline by
Catalytic Reforming (Performance Predicted by Correlations)

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FIGURE 4
HYDROTREATING OF
DEWATERED WHOLE SHALE OIL
3500-Hr Pilot Plant Test

Guard Bed - Alumina (Upstream from Catalyst)

Catalyst - ICR 106

Conditions

Target Product Nitrogen, ppm	500
H ₂ Pressure, psia	1600-2000
Catalyst Temperature, °F	760-800
LHSV	0.6

H₂ Consumption ~2000 SCF/Bbl at 2000 psia H₂

FIGURE 5
CONCLUSIONS
HYDROTREATING OF WHOLE SHALE OIL

1. Can denitrify to 1 ppm; 500-1500 ppm appears optimum.
2. Catalyst activity shows strong pressure dependence.
3. Fouling rate is very low at 2000 psia H_2 .
4. Can design for a commercial length run.
5. Guard bed successfully removes arsenic and iron.
6. Products similar to petroleum distillates.

FIGURE 6
COMPARISON OF 650-1000°F STRAIGHT-RUN VGO WITH
650°F+ HYDROTREATED SHALE OIL

<u>Inspections</u>	Arabian VGO	Hydrotreated Shale Oil	Sumatran VGO
	22.2 183 2.46 Wt % 780 1100 100	30.8 210 <10 ppm 870 200 100	31.9 217 1300 ppm 385 1000 110

FIGURE 7

HYDROFINISHING 350-650°F
HYDROTREATED SHALE OIL TO
DIESEL FUEL WITH ICR 106 CATALYST

Conditions: H₂ Pressure, psia - 1100
LHSV - 2.0

Chemical H₂

Consumption: < 100 SCF/Bbl

Catalyst Temp., °F	Feed	Product	
	-	650	710
<u>Inspections</u>			
Gravity, °API	37.4	37.6	37.9
Aniline Point, °F	149	151	151
Sulfur, ppm	40	40	20
Nitrogen, ppm	540	350	160
Pour Point, °F	0	-5	0
Thermal Stability Test*	Fail	Pass	Pass

* Accelerated Test for Diesel Stability

FIGURE 8

HYDROFINISHING 350-500°F
HYDROTREATED SHALE OIL TO
JET FUEL WITH ICR 106 CATALYST

Conditions: H₂ Pressure, psia - 1100
Catalyst Temp., °F - 729
LHSV - 2.0

Chemical H₂

Consumption: ~150 SCF/Bbl

Inspections	Feed	Product
Gravity, °API	41.2	42.0
Nitrogen, ppm	290	2
Freeze Point, °F	-37	-42
Smoke Point, mm	19	21
Gum, mg/100 ml	High	2
Group Type, LV %		
Paraffins	34	35
Naphthenes	40	44
Aromatics	26	21
95% Point by TBP Distillation, °F	502	508

*An end point of about 475°F is required for a -50°F freeze point.

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FIGURE 9

SINGLE-STAGE EXTINCTION
RECYCLE HYDROCRACKING OF
625-850°F HYDROTREATED SHALE OIL WITH
AGED ICR 106 CATALYST

Conditions: H₂ Pressure, psia - 2100
Catalyst Temp., °F - 785
LHSV - 1.0

Chemical H₂
Consumption: 1200 SCF/Bbl

Yields

C ₁ -C ₃ , Wt %	2.8
Isobutane, LV %	3.7
n-Butane, LV %	2.7
C ₅ -180°F, LV %	13.4
180-300°F, LV %	26.8
300-535°F, LV %	68.8
Total C ₅ ⁺ LV %	<u>109.0</u>

FIGURE 10
PROPERTIES OF JET PRODUCT FROM
HYDROCRACKING OF 625-850°F SHALE OIL

Boiling Range	300-535°F
Gravity, °API	47.6
Aniline Point, °F	167
Nitrogen, ppm	< 0.5
Group Type, LV %	
Paraffins	54
Naphthenes	41
Aromatics	5
Freeze Point, °F	-63
Smoke Point, mm	34
95% Point by TBP Distillation, °F	534

FIGURE 11
HYDROTREATING OF
SHALE OIL COKER DISTILLATE WITH
ICR 106

Conditions: H₂ Pressure, psia - 1500
 LHSV - 1.0

Catalyst Temperature, °F	718	733
Chemical Hydrogen Consumption, SCF/Bbl	1200	1250
Liquid Product Nitrogen, ppm	535	60
<u>Inspections</u>		
<u>180-350°F</u>		
Nitrogen, ppm	100	26
<u>350°F+</u>		
Nitrogen, ppm	630	68
Thermal Stability Test °	Pass	Pass
Pour Point, °F	+30	+30
<u>350-650°F</u>		
Pour Point, °F	+5	
<u>350-600°F</u>		
Pour Point, °F	-20	

• Accelerated Test for Diesel Stability

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FIGURE 12
COST SUMMARY
REFINING OF SHALE OIL

Products	Processing	Total Processing Cost, \$/Bbl of Product ²
100,000 BPCD Light Products ¹	Hydrotreating-Hydrocracking Hydrotreating Fluid Catalytic Cracking Delayed Coking-Hydrotreating	9.70 8.70 8.00
100,000 BPCD Hydrotreated Synthetic Crude	Hydrotreating	6.50

¹ Light products include LPG, motor gasoline, kerosene jet fuel, and diesel fuel (No. 2 oil).

² Based on estimated First Quarter 1978 costs, 15% rate of return on investment and 51% income tax.

ONR PROGRAMS IN COMBUSTION AND
CHEMICAL KINETICS

J. R. Patton, Jr.
(Office of Naval Research)

The two tasks constituting the ONR Air Breathing Propulsion Research Program are "Jet Propulsion Processes" (Project SQUID) and "Aircraft - Missile Satellite Propulsion". In both tasks, emphasis is on research support of the technology base for air-breathing engines, where the dynamic processes receiving emphasis, from the 6.1 standpoint, are common to both missile and aircraft applications. Complementary effort is conducted by NAVAIR to provide supporting research focused on critical propulsion flow problems and phenomena which are encountered in naval aero-propulsion systems. The objectives of those three tasks are shown on Chart 1.

Chart 2 illustrates the five areas of investigation constituting the current SQUID program. Two of these areas - "Combustion and Chemical Kinetics" and "Measurement Techniques" - are pertinent to the subject of this workshop. Under the Aircraft, Missile Propulsion Task, complementary research is conducted.

Combustion and Chemical Kinetics

Chart 3 depicts the six current research projects, under these tasks, that relate to combustion and kinetics. The technology drivers or objectives for these efforts are (a) the need for reduced fuel consumption (b) the need to develop alternate fuel capability, and (c) needed improvements in pollution and environmental characteristics.

In this area, previous effort involved molecular beam techniques for studies of rates and mechanisms of mass and energy transfer during gas-gas and gas-surface molecular collisions. This was of importance to evaporation and the thermodynamics of nucleation and condensation and the results have influence on propulsion efficiency by better characterization of the combustion processes.

In planning to make this research more relevant to what we believe to be research needs today, -- we held a workshop last September on the subject "Alternate Hydrocarbon Fuels for Engines: Combustion and Chemical Kinetics". In brief, its objective was to create a forum for discussion of the current status, anticipated problems, and research requirements relative to evolution of future fuel/engine systems under conditions of scarce petroleum supplies expected in the time period between 1990 and the year 2000. At that time, we described the situation to the attendees as follows:

- ° Use of synthetic fuels will be required in the future for both civilian and military applications.
- ° Engines must be designed and developed to operate on such fuels.
- ° A national policy is needed to develop these fuels.

As a result, we plan to give less emphasis to the following type efforts:

- ° Application of molecular beam techniques to the study of condensation and evaporation phenomena. (Except in the case of a break through).
- ° Aluminum and metal oxide reaction kinetics.
- ° Studies of chemical instabilities and chemical dynamics.

Long range goals will be:

- ° Control of physical-chemical characteristics of practical alternative fuels as they affect injection, ignition, flame development and local pollutant formation in gas turbine combustors.
- ° High and low temperature reaction kinetics of hydrocarbon of high aromatic content.
- ° Research on additives and catalytic agents for alternative fuels.

Charts 4 and 5 contain summaries of the Policy Questions and Research Areas which surfaced at the September workshop. The proceedings volume or text should be available by October.

The first project to be discussed has been active for two years. Dr. Dean of the University of Missouri is conducting a study using shock tubes of H_2 and CH_4 oxidation with N_2O as oxidant. The object is to more completely characterize combustion mechanisms by obtaining reliable high temperature values of rate constants. The need is for more reliable modeling studies of combustion processes. Dean has completed studies of the hydrogen system, which demonstrated that substitution of N_2O for O_2 was a viable technique for determination of high temperature rate constants of oxygen atoms. The rate constant for the reaction $H + N_2O = N_2 + OH$ over the temperature range 1950-2850°K was obtained. Work has started on the methanol system. In particular, data has been collected on the following:

$\text{CH}_4/\text{N}_2\text{O}/\text{CO}/\text{Ar}$

$\text{C}_2\text{H}_6/\text{N}_2\text{O}/\text{CO}/\text{Ar}$

$\text{CH}_2\text{O}/\text{N}_2\text{O}/\text{CO}/\text{Ar}$

$\text{CH}_2\text{O}/\text{Ar}$

Dr. Fenn has a program at Yale University on "Combustion Kinetics from Reactive Scattering Experiments". Under study is the reaction of hydrocarbons with oxygen by a molecular beam scattering experiment with the following features:

- (a) A high intensity beam from a nozzle source at temperatures high enough to provide substantial vibrational excitation in the molecular beam.
- (b) Cryogenic and/or absorptive trapping of scattered molecules over a long period of time to obtain high detection sensitivities.
- (c) Analysis of reaction products by gas chromatography.

Indications are that these experiments may permit the measurement of reaction cross sections smaller by several powers of ten than conventional scattering experiments using mass spectrometric detection - thus permitting possible identification of the individual steps in combustion reactions.

Dr. McLean's project, a new program at Cornell University, is titled "Pyrolysis of Synthetic Fuels using the Laser Homogeneous Pyrolysis Technique". The fuel pyrolysis involving high carbon-to-hydrogen ratio synthetic fuel is a problem of direct concern to the design and operation of future gas turbine engines. This new project is an experimental effort with emphasis on formation of soot precursors during pyrolysis. The technique is a relatively simple method of rapidly heating samples to temperature up to 1600°K . It is complementary to the single pulse shock tube method - but much simpler in that it covers a lower temperature range and generally longer reaction times. The technique involves a sample cell of about 5 cm^3 provided with infrared transparent windows and filled with a mixture of argon diluent, the desired reactants, and a small quantity of SF_6 . The sample is irradiated with infrared energy and the SF_6 with its fast vibration - translation relaxation time causes the sample to be heated to high temperatures in about 1 msec. For temperatures above the 1600°K , SiF_x would be used as the selective absorber.

Another new project, just approved, is at Kansas State University. Dr. T. W. Lester's project is titled "Isotopic Studies of the Chemical Mechanisms of Soot Nucleation". In this study, the characterization of isotopic compounds during the pyrolysis of simple hydrocarbons is expected to provide knowledge of the chemical reactions leading from the parent hydrocarbon to higher molecular weight products which precede soot formation. Primary motivation of this work is a desire to better understand the early stages in the formation of high molecular weight hydrocarbon from simpler hydrocarbons such as methane.

The next project is at Princeton University. Here, Professor Sirignano is conducting fundamental studies of turbulent, swirling, jet ignition. The effect of swirl on turbulent mixing has remained a controversial but important subject over the years. It is hoped here to elucidate the role of swirl on large scale structures in turbulent flows and its effect on the detailed mixing process. Smoke and LDV diagnostics will be utilized.

Another new project is that of Dr. E. T. McHale (Atlantic Research Corporation) on the "Chemistry of Combustion of Fuel-Water Mixtures." At the Project SQUID Workshop on Alternative Hydrocarbon Fuels, discussions revealed the fundamental importance of water chemistry to (a) the performance of synthetic fuels in general and (b) the control of synthetic fuels in general, and (c) the control of soot production, especially when high aromatic-content fuels are used by themselves and when water is added to the fuels. The effects of water addition to practical combustors is important not only with respect to current petroleum fuels but probably more so with future alternative fuels with greater aromatic content and their higher sooting and radiation tendencies. Suppression of soot by water addition is mainly a chemical effect and it is not well understood. The fundamental question is the formation of carbon in a form that will lead to soot formation. Once carbon formation can be understood, the growth of a carbon particle due to various physical-chemical processes can be modeled. The proposed work will be an experimental flame structure study utilizing a diffusion flame using pure fuel gases or vapors. To establish the technique, low molecular weight paraffin will be studied (probably methane or ethane and acetylene). Liquid fuels will be investigated, including straight and branched chain aliphatics, and aromatics up to substituted polycyclics. Fuels with present-day military interest will be investigated such as the JP fuels up to JP8, Jet A, alternates, etc. Water vapor (and other additives such as CO_2 , O_2 , and CH_3OH) will be added to the fuel side of the flame at various concentrations. It is known that water and CO_2 reduce soot, whereas very small additions of oxygen to a gaseous fuel promote soot formation. When chemical reasons for these effects become better understood, it will hopefully be possible to design cleaner and

more efficient combustion systems with improved burning of low-grade oils and future synthetic fuels. These objectives have particular importance to optimum jet engine performance, engine life and reliability.

Measurement Techniques

Following an early workshop on "Gas Dynamics Research", we have given some emphasis to optical techniques to measure flow properties (velocity, temperature, concentration) in flows where classical probes would be destroyed by centrifugal forces (rotors) or high temperatures (combustors). Under this program, there has been extensive development of Raman techniques including spontaneous Raman scattering. CARS, and Ramanography for application in combustion and reactive environments. Current long range goals are:

- (a) In-situ measurements of particle size and velocity distribution in developing environments with liquid droplets and solid particles.
- (b) Nonintrusive measurement of steady, nonsteady and turbulent quantities (temp. and concentration) in chemically reactive systems with incomplete combustion and nonequilibrium chemical processes.
- (c) Synthesis of nonintrusive measurement techniques (SRS, CARS, fluorescence, induced scattering) with a delineation of the manner in which they can be used in a complementary fashion in any given situation.

6.1 AIR BREATHING TASK OBJECTIVES

CNR

JET PROPULSION PROCESSES (PROJECT SQUID)

To provide an understanding of the Chemical and Flow Processes useful in supporting and expanding the Navy's technology base for design and development of Jet Engines.

AIRCRAFT, MISSILE, SATELLITE PROPULSION

To improve propulsion systems, and develop enlightened understanding on an interdisciplinary basis, of engine concepts useful to design and development of high power, reliable Jet Engines.

NAVAIR

AIRCRAFT, MISSILE, SATELLITE PROPULSION

Research focussed on the reduction and elimination of potential development problems in NAVAIR propulsion systems, and leading toward improved prediction and design procedures.

CHART 1

PROJECT SQUID

1977-1978

PRINCIPAL AREAS OF RESEARCH

Fluid Mechanics and Gas Dynamics	19% 4 subcntrs.
Turbomachinery and Diffusers	22% 4 subcntrs.
Turbulent Mixing Phenomena	26% 8 subcntrs.
Measurement Techniques	20% 5 subcntrs.
Combustion, Chemistry and Chemical Physics	<u>13%</u>	<u>.... 6 subcntrs.</u>
	100%	27

CHART 2

COMBUSTION AND KINETICS PROJECTS

PROJECT SQUID

UNIV. MISSOURI

YALE UNIVERSITY

CORNELL UNIV.

PRINCETON UNIVERSITY

KANSAS STATE UNIV.

RATE CONSTANTS-SHOCK TUBE STUDIES

COMBUSTION KINETICS

PYROLYSIS OF SYNTHETIC FUELS

SWIRLING, JET IGNITION

SOOT NUCLEATION

AIRCRAFT, MISSILE PROPULSION

ATLANTIC RESEARCH CORP.

WATER ADDITION-CHEMISTRY OF COMBUSTION

ALTERNATIVE FUELS

POLICY QUESTIONS

- WHAT IS THE BASIS FOR EVOLVING A SIGNIFICANT POLICY ON ALTERNATIVE FUELS FOR AIRCRAFT IN THE DOD? GUARANTEED PRICE?
- HOW SHOULD WE CONDUCT RESEARCH ON ALTERNATIVE FUELS WITH THE RIGHT INTERACTION BETWEEN PRODUCTION AND COMBUSTION PROCESSES?
- WHAT IS THE METHOD OF ESTABLISHING THE MINIMUM PRODUCTION AND COMBUSTION EXPERIMENTAL STUDIES THAT CAN BE EFFECTIVE?
- RESEARCH NEEDS:
 - I) BALANCED POLICY ON FUELS
 - II) THERMAL STABILITY
 - III) UTILIZATION TECHNOLOGY
 - IV) COMBUSTION AND ENVIRONMENT
 - V) PRODUCTION PROBLEMS (CONFLICTS IN ESTABLISHING CUTS)
 - VI) LIQUID FUEL TECHNOLOGY (COST OF PRODUCTION AND COST OF REPLACEMENTS)
- HOW DO WE GO FROM BASIC RESEARCH TO APPLICATIONS IN THIS AREA? IN OTHER WORDS, HOW DO WE ESTABLISH RESEARCH PROJECTS AT THE PROPER INTERMEDIATE (APPLICATION) LEVEL?

ALTERNATIVE FUELS

RESEARCH AREAS

- PHYSICAL CHARACTERISTICS AND INJECTION AND ATOMIZATION STUDIES.
- LOW TEMPERATURE OXIDATION CHARACTERISTICS AND DEPOSITS.
- IGNITION CHARACTERISTICS.
- SOOT FORMATION INCLUDING NUCLEATION AND AGGLOMERATION.
- RADIATION FROM FLAMES.
- CHEMICAL KINETICS

- PYROLYSIS AND OXIDATION
- RATE DATA FOR SO_x REACTIONS
- HETEROGENEOUS CATALYSIS
(SURFACE CHEMISTRY)
- COMBUSTION OF LEAN MIXTURES
- HYDROPEROXYL RATES
- ADDITIVES TO FUELS FOR
CONTROL OF LOW AND HIGH
TEMPERATURE OXIDATION
- QUENCHING KINETICS
- THERMAL INSTABILITY PROBLEM.
- RATE DATA FOR NO OXIDATION

FUEL PROPERTY STUDIES

ALBERT ANTOINE

(NATIONAL AERONAUTICS AND SPACE
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FUEL PROPERTY STUDIES AT NASA-LEWIS

Fuel property studies are performed in three different sections of a Fuels Technology Branch: Fuels Combustion, Fuels Systems, and Physical Chemistry. A general description of the work of each section is shown in Figure 1, covering programs with combustors, fuels, fuel systems, and combustion fundamentals and analysis. Figure 2 gives the overall objective of the fuels technology branch, which involves the evaluation of the characteristics of future jet aircraft hydrocarbon fuels, the determination of their effects on engine components, and the development of required component technology.

The overall program is designed to include the recommendations generated in the recent workshop held at the Lewis Research Center (June 7-9, 1977) (Ref. 1). The major recommendations from that workshop are given in figure 3. Trade-off and cost effectiveness studies are recommended in regard to broad specification fuels, in addition to combustor technology and fuel systems simulator tests with these fuels. Some details of the approach to be taken to meet the objectives of the program are given in figure 4. An in-house hydrotreating facility for the preparation of fuels from oil shale and coal syncrudes is finished and is undergoing shakedown tests. In addition to these fuels, petroleum based fuels meeting the suggested broad specification requirements will also be examined. The chemical composition will be determined and related to the observed properties. Work will continue on energy optimization studies using the computer model developed (under contract) for refinery operations with emphasis on jet fuel production (ref. 2). Work is being planned for fundamental studies on the mechanisms and kinetics of soot formation and fuel degradation. Work has already started on determining

the effects of varying fuel properties on combustor performance. In an in-house program (ref. 3) a single-can combustor was investigated with a number of fuels exhibiting wide variations in chemical composition (hydrogen content from 11.0 to 15.3 percent) and volatility (up to 635°F). Pronounced effects of changes in fuel composition were observed at simulated cruise and take off conditions where smoke and liner temperatures increased significantly as the hydrogen content of the fuel decreased. Combustion efficiencies were 99.9 percent or above for all of the fuels. At simulated idle condition, no significant effects of fuel quality on combustor performance were observed. In the fuel system research and technology area, attention is being given to the problems expected with fuels of higher freezing point. An analytical airframe fuel system study of high freezing point fuels (-20°F, 0°F) was recently completed under contract (ref. 4).

Figure 5 describes some current program activities in fuels synthesis and characterization. In addition to in-house laboratory studies, the contract and grant activities are listed. The work at UCLA presents the conceptualization and initial development of a decision model for predicting the future availability and characteristics of aviation fuels (ref. 5).

The objective of the research program at the Colorado School of Mines is to determine the effect of concentration of various types of nitrogen-containing compounds on the thermal stability of aircraft turbine type fuels. To measure the effect, samples of Jet A fuel are being spiked with an extract from an oil shale syncrude. Both storage and thermal stability tests are being made on such spiked fuels. This work is being complemented with JFTOT studies at Lewis with Jet A fuels doped with known amounts of single compounds, and mixtures of known compounds.

In Figure 6 the combustor research and technology activities in re-

gard to broadened specification fuels are listed. Combustor concept evaluations are in progress, and a flame radiation study will be initiated. Contract work in this area will not be discussed here, with the exception of the soot formation study. This research is being conducted at MIT under an NASA University grant program. The purpose of the research is to develop an understanding of the mechanism of soot formation in jet engines, with a long range goal of developing a simple, semi-empirical model of soot formation and burnup which can be used to predict the amounts of soot occurring in a full scale combustor. Approximately equal effort will be placed on turbulent mixing studies, fuel composition, and stoichiometry.

In the fuel system research and technology area, figure 7, attention is being given to the problems expected with fuels of higher freezing point, and a study of fuel heating system designs is in progress. It is planned to experimentally evaluate such heating systems using a fabricated subscale airframe/engine system. In another study, a subscale tankage system representative of commercial jet aircraft practice will be fabricated. The system will be used to gain an understanding of the relationship between practical pumpability of aircraft jet fuels and the various specification tests related to freezing point. From this understanding, a set of reproducible pumpability criteria may be established. To address another major problem expected with broad-specification fuels, thermal stability, a facility simulating an aircraft fuel system will be fabricated. The apparatus will be larger than present laboratory models by an order or two of magnitude. The purpose of the proposed studies is to examine the effect of some variables on hydrocarbon fuel thermal stability, and establish criteria for quantitative assessment of fuel thermal degradation. An RFP for this work has been issued.

A number of accomplishments reported in the last year are summarized in figure 8. The jet aircraft synfuels were prepared under contract (ref. 6), and the specifications for the experimental, referee, broad-specification fuel were generated from suggestions given at the workshop (ref. 1). The specifications for the proposed fuel are given in figure 9. The fuel was designed particularly for combustion system research by control of fuel composition, and felt to be reasonably easy to supply, and adequately reproducible in regard to combustion characteristics. Figure 10 shows the variation of breakpoint temperature with nitrogen content for a number of fuels derived from shale oil. An improved stability with reduced nitrogen content is evident, but it is realized that the increased hydrogenation severity that was required to reduce the nitrogen content also reduced the concentrations of other species that might be as much or more responsible for the instability. Figure 11 shows some results obtained under the MIT grant program using a laboratory turbulent diffusion flame burner. The type of fuel used makes a significant difference, and blends of benzene and n-heptane were used to simulate a range of hydrogen concentrations. In other burner tests the effect of the hydrogen content of the fuel on liner temperatures was determined. Figure 12 shows the results from a single-can JT8D combustor, with significant increases seen with a decrease in hydrogen content. Figure 13 shows similar results, first with conventional combustor liners, then with the experimental Vorbix and double-annular combustors, the latter two showing a relative insensitivity to the hydrogen content. Another method of reducing liner temperatures consists of coating the inside of the combustor liner with a thermal-barrier coating. Shown in figure 14 are the results obtained with Jet A fuel, showing substantial reductions in maximum liner temperatures for both cruise and takeoff. For

these tests a JT8D combustor liner was coated with a thermal-barrier coating developed at the Lewis Research Center for application to turbine blades (ref. 7).

The last item in the list of accomplishments refers to the work completed under the Boeing contract, in which fuel system modifications were examined for the solution of high-freezing-point problems. Fuels with higher freezing points than those with the current specifications can be used if the fuel is heated in flight. Figure 15 shows 3 curves of predicted fuel temperatures during a long range flight. With no heat input the minimum fuel temperature reaches -46°F . The minimum fuel temperature in flight can be raised to -20°F by heating the fuel at a rate of 3500 BTU/min, or to 0°F by heating at a rate of 6200 BTU/min. A preliminary study of practical fuel heating systems based on the 747 airplane was also completed, and several possible heat source systems were identified. These are shown in figure 16. With just minor modifications three existing components can be used as heat sources: the cabin air-conditioning heat rejection, fuel recirculation from the fuel pump, and the fuel recirculation from the engine lubricating oil heat exchanger. With major modifications, three others could be used. These are the tailpipe heat exchanger, an engine compressor air bleed heat exchanger, and an electrical heater powered by an engine-drive generator.

In summary, Figure 17 shows some specific plans for the coming year in the areas of fuels synthesis and characterization, combustion fundamentals, combustor research and technology and fuel system research and technology for broadened specification fuels.

REFERENCES

1. NASA Conference Publication 2033. Jet Aircraft Hydrocarbon Fuels Technology. 1978
2. Daniel N. Dunbar, Barry G. Tunnah, Computer Model for Refinery Operations with Emphasis on Jet Fuel Production. NASA CR-135333 Feb. 14, 1978
3. Helmut F. Butze and Arthur L. Smith. Effect of Fuel Properties on Performance of a Single Aircraft Turbojet Combustor at Simulated Idle, Cruise, and Take Off Conditions. NASA TM-73780, September 1977
4. A. J. Pasion, I. Thomas. Preliminary Analysis of Aircraft Fuel Systems for Use With Broadened Specification Jet Fuels. NASA CR-135198, June 1977
5. J. M. English, C. Y. Liu et al. Forecast of Future Aviation Fuels Part I: Scenarios. UCLA-ENG 77-78, November 1977
6. Synthesis and Analysis of Jet Fuel from Shale Oil and Coal Syncrudes. J. P. Gallagher, T. A. Collins, T. J. Nelson, M. J. Pedersen, M. G. Robison, L. J. Wisinski. NASA CR-135112 November 17, 1976
7. Butze, Helmut F. and Liebert, Curt H.: Effect of Ceramic Coating of JT8D Combustor Liner on Maximum Liner Temperatures and Other Combustor Performance Parameters. NASA TM X-73581, 1976

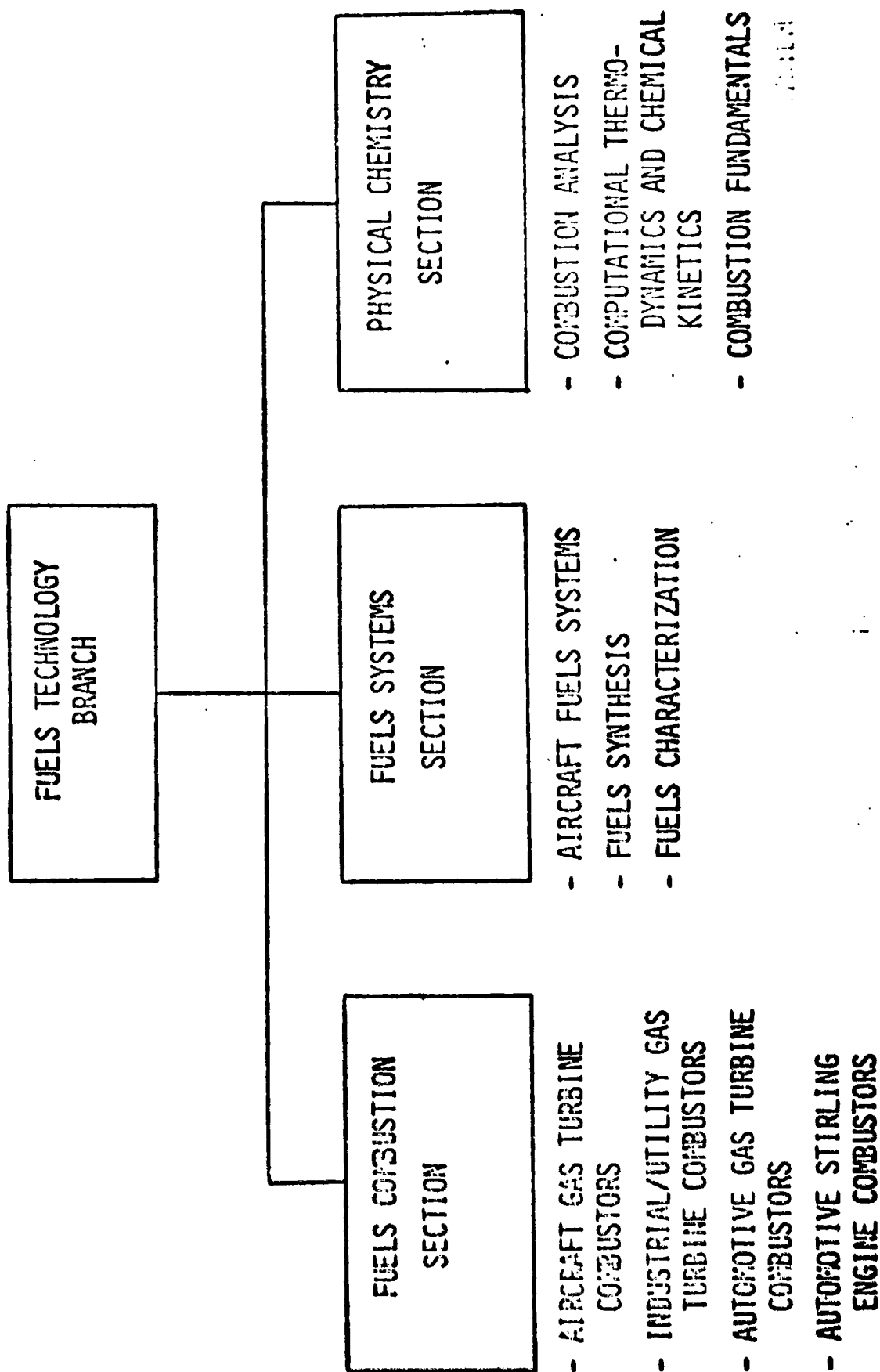


FIG. 1

FUELS RESEARCH

OBJECTIVE:

EVALUATE THE POTENTIAL CHARACTERISTICS OF FUTURE JET AIRCRAFT FUELS, DETERMINE EFFECTS ON ENGINE COMPONENTS AND EVOLVE COMPONENT TECHNOLOGY

APPROACH:

- IDENTIFY PROBABLE PROPERTIES OF FUTURE ALTERNATIVE AVIATION TURBINE FUELS REFINED FROM EITHER PETROLEUM, SHALE OIL OR COAL SYNCRUDE
- ESTABLISH FUNDAMENTAL DATA BASE ON THERMODYNAMICS AND CHEMICAL KINETICS OF COMBUSTION AND FUEL DEGRADATION REACTIONS
- DETERMINE EFFECTS OF RELAXING FUEL SPECIFICATIONS ON COMBUSTOR PERFORMANCE, EMISSIONS, AND DURABILITY: AND EVOLVE COMBUSTOR TECHNOLOGY FOR BROAD SPEC. FUELS
- DETERMINE THE EFFECTS OF RELAXING FUEL SPECIFICATIONS ON FUEL SYSTEM PERFORMANCE AND DURABILITY AND ON ENGINE MATERIALS SUCH AS FUEL SYSTEM ELASTOMERS AND HOT SECTION ALLOYS AND COATINGS, AND TO EVOLVE AND EVALUATE TECHNOLOGY FOR BROAD SPEC. FUELS

Fig. 2

MAJOR RECOMMENDATIONS FROM "WORKSHOP ON JET AIRCRAFT HYDROCARBON FUELS TECHNOLOGY"

- PERFORM MORE EXTENSIVE TRADE-OFF & COST EFFECTIVENESS STUDIES OF OVERALL FUEL REFINERY-DISTRIBUTION-AIR TRANSPORTATION SYSTEMS.
- EXPAND COMBUSTOR TECHNOLOGY EFFORT FOR OBTAINING ACCEPTABLE LINER TEMPERATURES, IGNITION/RELIGHT, AND EMISSIONS USING BROAD-SPEC FUELS.
- EXTEND CURRENT STUDIES ON HIGH-FREEZING POINT FUELS AND LOW-TEMPERATURE PUMPABILITY TO FULL-SCALE FUEL SYSTEM SIMULATOR TESTING.
- RELATE LABORATORY THERMAL STABILITY MEASUREMENTS TO ACTUAL DEPOSIT FORMATION RATES IN FUEL INJECTORS & FUEL MANIFOLDS.

FIG. 3

APPROACH

FUELS SYNTHESIS & CHARACTERIZATION

- SYNTHESIZE AND CHARACTERIZE JET FUEL FROM "SYNTHETIC" CRUDES
- DETERMINE EFFECTS OF CHEMICAL COMPOSITION ON FUEL CHARACTERISTICS
- ANALYZE EFFECTS OF VARYING FUEL SPECIFICATIONS ON REFINERY ENERGY CONSUMPTION AND COST

COMBUSTION FUNDAMENTALS

- CONDUCT ANALYTICAL AND EXPERIMENTAL STUDIES TO DETERMINE EFFECTS OF FUEL PROPERTIES ON SOOT FORMATION AND FUEL DEGRADATION

COMBUSTOR R & T - BROAD-SPEC FUELS

- DETERMINE EFFECTS OF VARYING FUEL PROPERTIES ON COMBUSTOR PERFORMANCE
- DESIGN AND EVALUATE COMBUSTOR CONCEPTS FOR BROAD-SPECIFICATION FUELS

FUEL SYSTEM R & T - BROAD-SPEC FUELS

- DETERMINE EFFECTS OF VARYING FUEL PROPERTIES ON PERFORMANCE OF AIRCRAFT FUEL SYSTEM
- DESIGN AND EVALUATE AIRCRAFT FUEL SYSTEMS FOR BROAD-SPECIFICATION FUELS

CURRENT FUELS TECHNOLOGY PROGRAM ACTIVITIES

FUELS SYNTHESIS AND CHARACTERIZATION

IN-HOUSE

- o LABORATORY STUDIES OF SYN-FUELS

CONTRACT/GRAANT

- o AVIATION FUELS FORECAST (UCLA)
- o REFINERY COMPUTER MODEL STUDY (GORDIAN ASSOC.)
- o STUDY OF NITROGEN-CONTAINING FUELS (COLORADO SCHOOL OF MINES)

FIG. 5

CURRENT FUELS TECHNOLOGY PROGRAM ACTIVITIES

COMBUSTOR R & T - BROAD. SPEC. FUELS

IN-HOUSE

- COMBUSTOR CONCEPT EVALUATIONS
- FLAME RADIATION STUDY

CONTRACT/GRANT

- COMBUSTOR DESIGN STUDIES (G. E., P & W)
- COMBUSTOR PRIMARY-ZONE TECHNOLOGY
- LOW-POLLUTANT ENGINE EVALUATIONS (G. E., AIRESEARCH)
- SOOT FORMATION STUDY (MIT)

CURRENT FUELS TECHNOLOGY PROGRAM ACTIVITIES

FUEL SYSTEM R & T - BROAD. SPEC. FUELS

CONTRACT

- o FUEL SYSTEM DESIGN STUDY (BOEING)
- o LOW-TEMPERATURE FUEL SYSTEM STUDY (LOCKHEED)
- o FUEL SYSTEM - THERMAL STABILITY STUDY

ACCOMPLISHMENTS (FY 1977/78)

FUELS SYNTHESIS & CHARACTERIZATION

- SYNTHESIZED JET AIRCRAFT SYNFUELS FROM SHALE OIL AND COAL SYNCRUDES
- ESTABLISHED SPECIFICATIONS FOR EXPERIMENTAL REFERENCE BROAD-SPEC FUEL
- CORRELATED THERMAL STABILITY OF SYNFUELS WITH CHEMICAL COMPOSITION

COMBUSTION FUNDAMENTALS

- OBTAINED FUNDAMENTAL DATA ON EFFECT OF FUEL PROPERTIES ON SOOT FORMATION RATES

COMB. R & T - BROAD-SPEC FUELS

- EVALUATED EFFECTS OF VARYING FUELS PROPERTIES ON A CONVENTIONAL COMBUSTOR LINER AT SIMULATED OPERATING CONDITIONS
- EVALUATED EFFECTS OF VARYING FUEL PROPERTIES ON LOW-POLLUTANT COMBUSTORS AT SIMULATED OPERATING CONDITIONS
- EVALUATED THE EFFECT OF CERAMIC THERMAL BARRIER COATING ON A CONVENTIONAL COMBUSTOR LINER

FUEL SYS. R & T - BROAD-SPEC FUELS

- PERFORMED ANALYTICAL STUDY OF EFFECT OF HIGH FREEZING POINT FUELS ON THE DE-
- - - SIGN OF THE AIRCRAFT FUEL SYSTEM

FIG. 8

PROCESSED EXPERIMENTAL REFERENCE BROAD-SPECIFICATION AVIATION TURBINE FUEL

HYDROGEN , WT. %	12.8 ± 0.2
SULFUR, TOTAL, WT. %	0.3 MAX
FLASH POINT, °F	110 ± 10
10% DISTILLATION TEMP., °F	400 MAX
90% DISTILLATION TEMP., °F	500 MIN.
FREEZING POINT, °F	-20 MAX.
VISCOSITY, @ -10°F, CS	12 MAX.
THERMAL STABILITY, JFTOT BREAKPOINT TEMP., °F	460

FIG. 9

VARIATION OF BREAKPOINT TEMP. WITH NITROGEN LEVEL

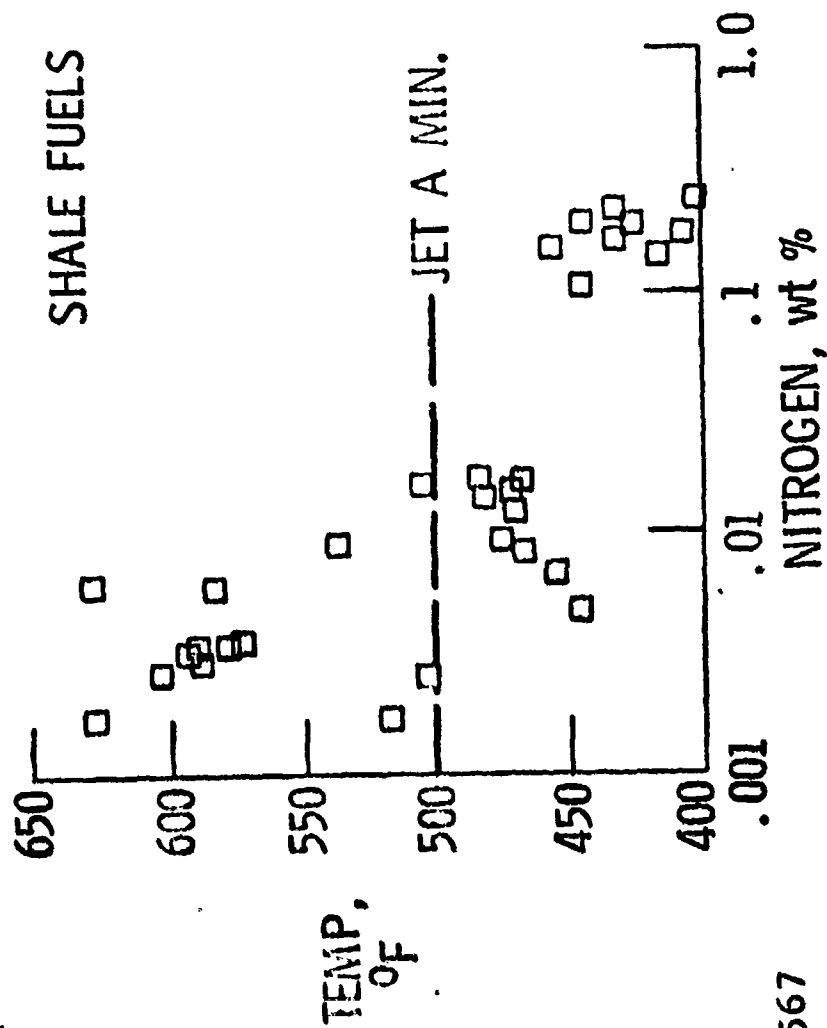


FIG. 10

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EFFECT OF HYDROGEN ON PEAK SOOT CONCENTRATION

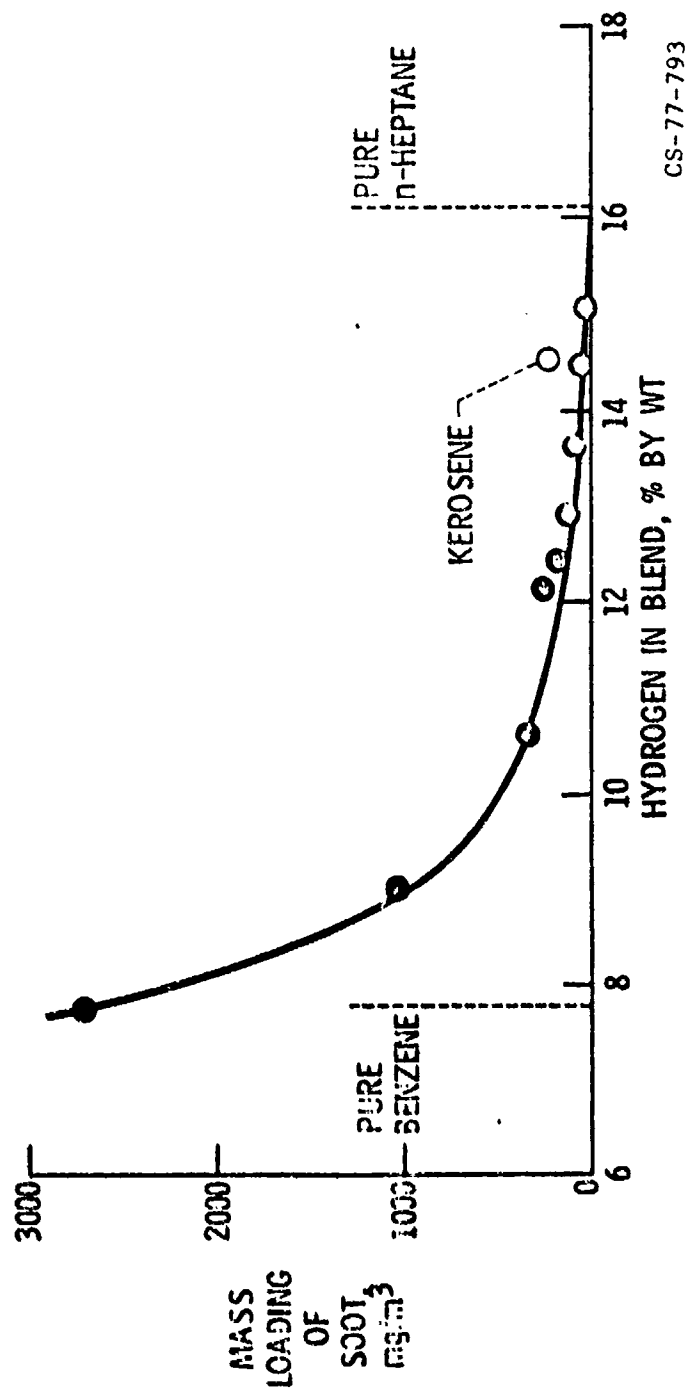
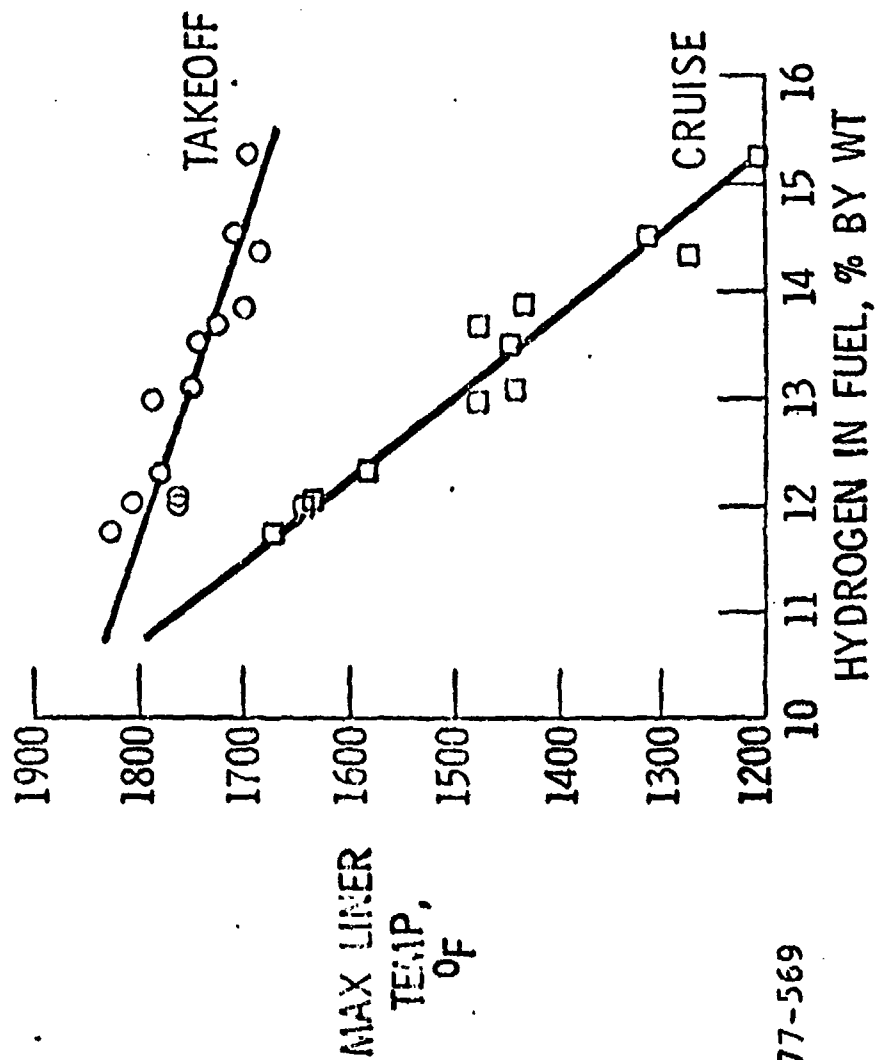


FIG. 11

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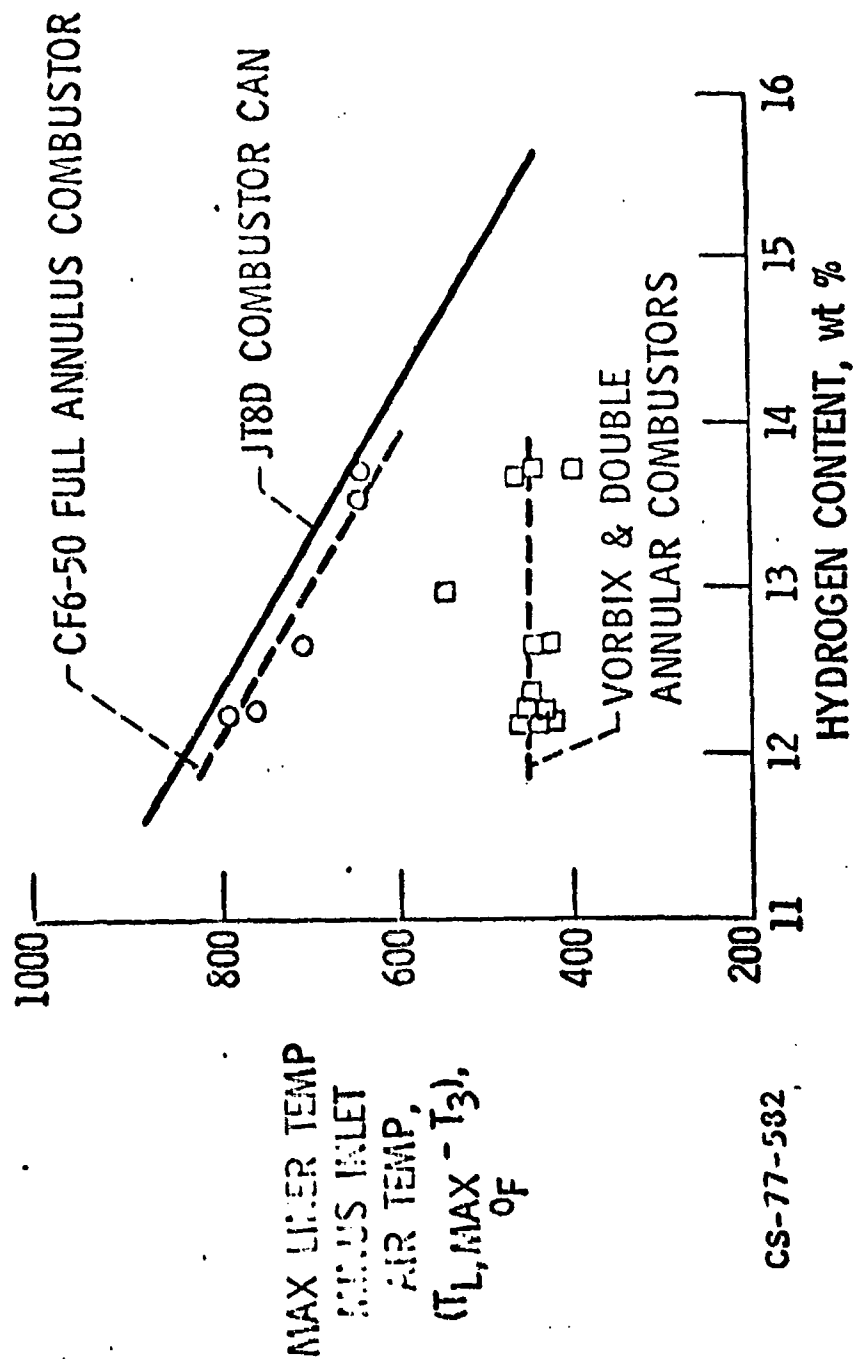
EFFECT OF HYDROGEN CONTENT OF FUEL ON MAXIMUM LINER TEMPERATURES



CS-77-569

FIG. 12

EFFECT OF HYDROGEN CONTENT OF FUEL ON COMBUSTOR LINER SURFACE TEMPERATURE



CS-77-532

FIG. 13

EFFECT OF CERAMIC COATING ON MAXIMUM LINER TEMPERATURE

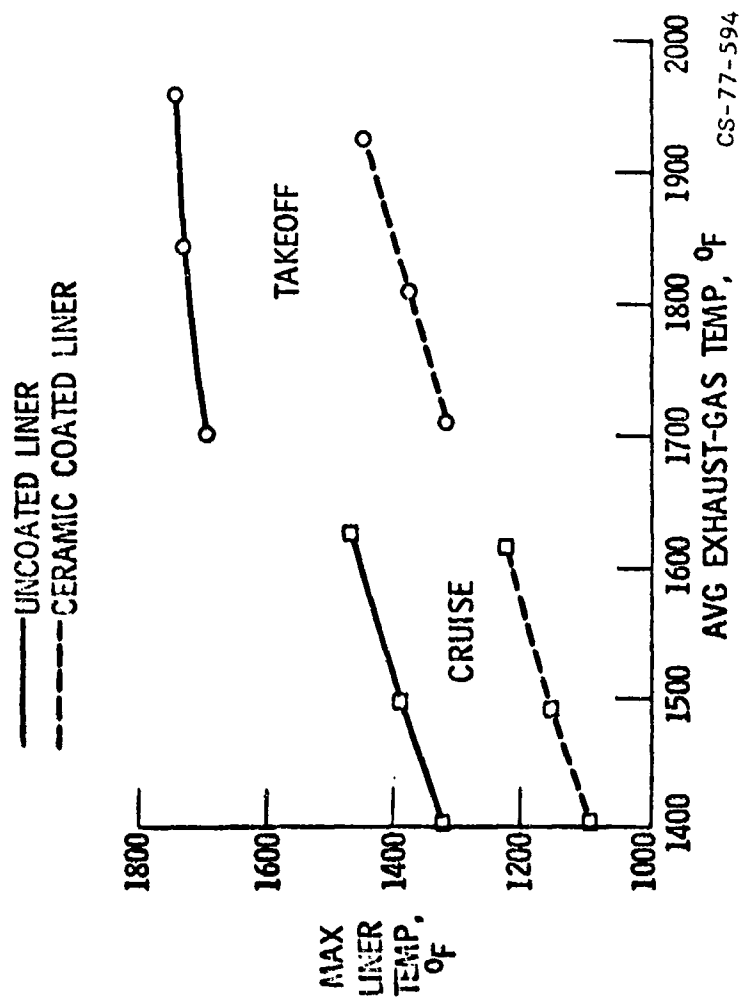


FIG. 14

FUEL TANK TEMPERATURES FOR 5000 N.M. FLIGHT WITH HEATING

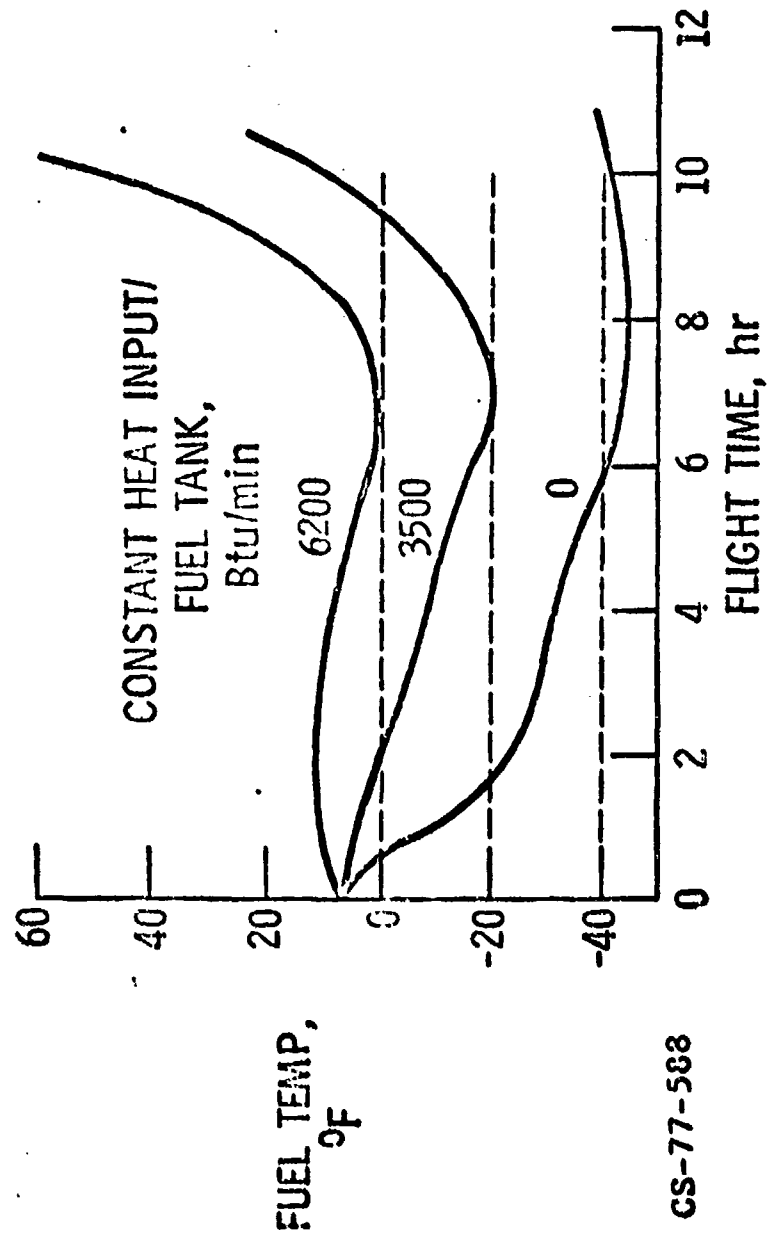
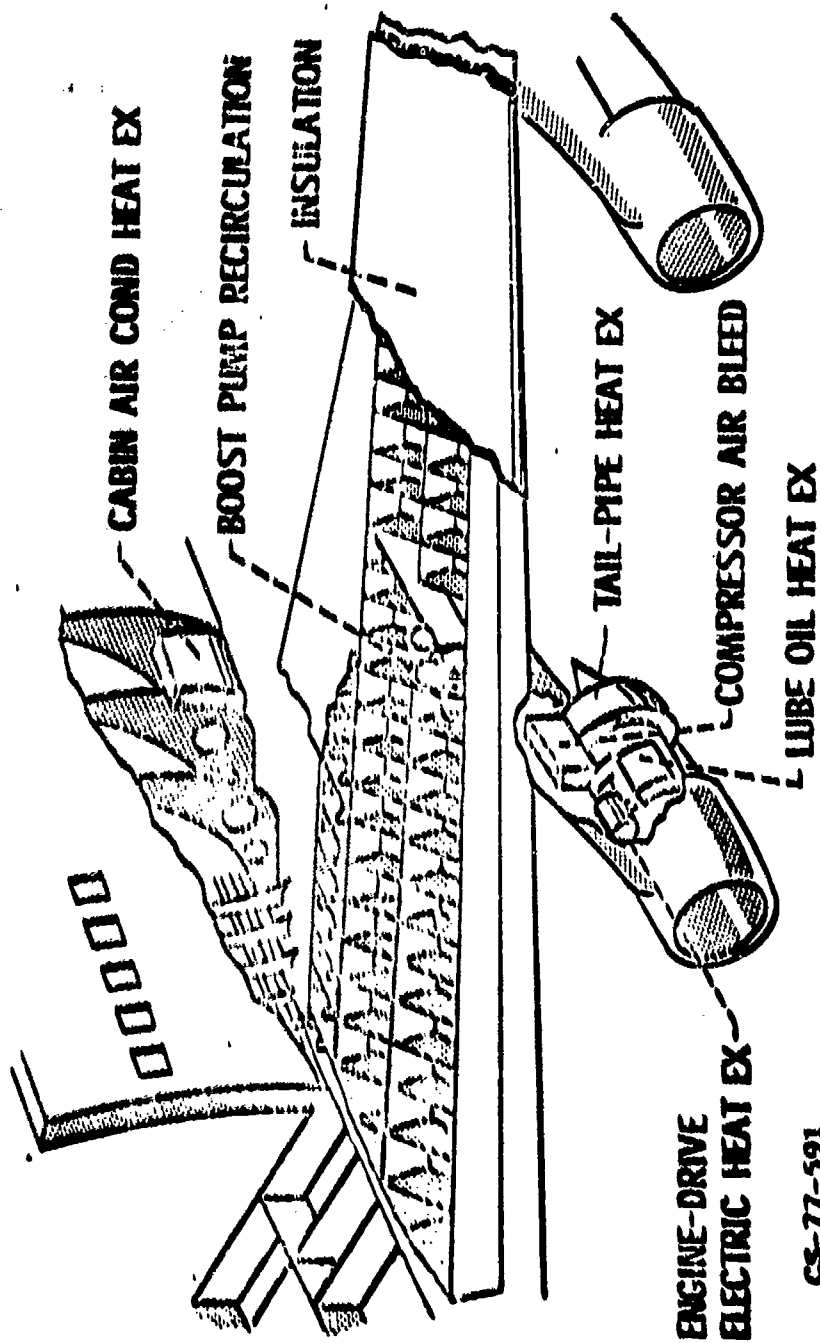


FIG. 15

CS-77-588

FUEL TANK HEATING SOURCES



CS-77-591

FIG. 16

PLANS FOR FY 1979

FUELS SYNTHESIS & CHARACTERIZATION

- COMPLETE STUDY ON EFFECT OF VARYING NITROGEN REMOVAL ON PROPERTIES OF "PARAHO" SHALE OIL DERIVED JET FUELS
- COMPLETE PRELIMINARY ANALYSIS ON EFFECT OF CRUDE PROPERTIES AND JET FUEL SPECS ON REFINERY ENERGY CONSUMPTION
- INITIATE STUDY ON EFFECT OF FUEL COMPOSITION ON FREEZING POINT AND VISCOSITY

COMB. FUEL.

- CONTINUE STUDIES ON EFFECT OF FUEL COMPOSITION ON SOOT FORMATION
- INITIATE FUNDAMENTAL STUDIES ON COMBUSTION AND FUEL DEGRADATION REACTIONS

COMB. R & T - BROAD-SPEC FUELS

- CONTINUE EVALUATION OF COMBUSTOR CONCEPTS FOR BROAD-SPEC FUELS
- COMPLETE DESIGN AND INITIATE FABRICATION OF A HIGH-PRESSURE COMBUSTOR RIG FOR STUDY OF BROAD-SPEC FUELS
- COMPLETE DESIGN AND INITIATE PROCUREMENT OF REFURBISHED HEAT EXCHANGER FOR COMBUSTOR TESTING

FUEL SYS. R & T - BROAD-SPEC FUELS

- COMPLETE CONCEPTUAL DESIGNS OF FUEL HEATING SYSTEMS FOR 747 AND E³ AIRCRAFT
- COMPLETE EXPERIMENTAL STUDY OF FUEL FLOW CHARACTERISTICS AT LOW TEMPERATURES
- COMPLETE FABRICATION OF REDUCED-SCALE AIRCRAFT FUEL SYSTEM FOR STUDY OF FUEL THERMAL STABILITY
- INITIATE EXPERIMENTAL EVALUATION OF A FUEL HEATING SYSTEM

FIG. 17

THERMAL OXIDATIVE STABILITY OF
SYNTHETIC JET FUELS

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Introduction: This presentation is part of the work conducted at the Naval Air Propulsion Center (NAPC) directed towards the study of the application of synthetic fuels for Navy aircraft use. The overall program objective is to establish the physical and chemical suitability of JP-5 derived from alternate (non-petroleum) sources for aircraft propulsion systems. The objective of this particular work is to establish a relationship between the organic nitrogen content and the thermal oxidation stability and storage stability of jet fuel derived from oil shale. The importance of this work is to obtain some knowledge of the effects of nitrogen on these properties since there is currently no specification requirement for the control of nitrogen in the JP-5 specification (3).

The fuel used in this study was derived from shale oil crude produced by the Paraho Process. The crude was refined in April 1975 by the Gary Western Refinery, Fruita, Colorado.

All of the thermal oxidation determinations made on the various fuels were performed with the Alcor Jet Fuel Thermal Oxidation Tester, coined the JFTOT. This is a standard ASTM test for evaluating fuel thermal oxidation behavior. The procedure is described by the ASTM D-3241 test outline. The criteria used for evaluating the deposition tendencies of a thermally stressed fuel are as follows:

(1) The deposit formed on the heated aluminum surface shall not exceed a spun deposit rating (TDR) of 17, as determined by the light reflectance device Alcor Mark 8A, tube deposit rater.

(2) The deposits formed in the bulk fuel that have not collected on the heated surface are trapped downstream by a filter at the fuel outlet of the preheater section. When a pressure drop of 25 millimeters is observed the fuel will be classified as thermally unacceptable. Once this pressure level has been reached, the JFTOT is put into a by-pass mode which essentially eliminates the fuel passage through the filter. The time to reach the by-pass mode is recorded (4).

The first determination made on the effects of fuel bound nitrogen on thermal oxidation stability was made by varying the acid extractable

*(Numbers in parentheses refer to figures at end of the paper).

nitrogen concentration of the fuel, and then determining the breakpoint temperature in the JFTOT. The fuel samples were prepared as follows:

(1) A shale oil JP-5 containing 954 ppm total nitrogen was extracted by 0.1 N HCl. After neutralization with sodium bicarbonate and water washing the fuel contained 116 ppm total nitrogen, which could not be removed by acid extraction.

(2) The above fuel was then blended with the unextracted fuel containing the original 954 ppm nitrogen until the desired nitrogen concentration was reached. The basic nitrogen content was determined on each blend using the perchloric acid titration method. The non-basic nitrogen concentration was constant in all samples (5).

A breakpoint temperature determination on the fuels revealed that there was a relationship between the basic nitrogen content and the type of JFTOT failure observed. It was quite apparent that the basic nitrogen produced a greater difference in the breakpoint temperature using the pressure drop criterion than the deposit level on the heater tube. That is, a basic nitrogen concentration range of 7 to 838 ppm produced a 52°C difference in the breakpoint based upon filter drop, whereas, only a 10°C difference was observed with using the heater tube failure criteria (6).

In further pursuance of the effect of nitrogen, particularly the acid extractable type, work was continued with a petroleum derived fuel, which was essentially nitrogen free. The basic nitrogen that had been isolated was added into this fuel at various concentrations and a JFTOT determination was made at a constant test temperature of 260°C (7). This temperature is the current requirement for a fuel to pass according to the ASTM instructions and MIL-T-5624K for grades JP-4 and JP-5 fuel.

The results of the test showed that the fuel could probably tolerate a nitrogen concentration of the order of 100 ppm if the JFTOT thermal stability rating criteria were based solely on deposits forming on a heated surface. However, using the pressure drop criteria the nitrogen concentration must be less than 50 ppm (8) to obtain a pass rating for the fuel. With regards to the preheater section, responses to changes in nitrogen concentration were somewhat unusual and unexpected. The TDR increased as a function of the nitrogen content up to 300 ppm. The higher concentrations, 400 and 500 ppm nitrogen, produced TDR's equivalent to 50 and 100 ppm. A close inspection of the total TDR on the heater tube reveals that beyond 300 ppm the nitrogen compounds in the fuel are producing deposits in the bulk fuel at the cooler section of the JFTOT (9). This is also observed by the decrease in time for the filter section to be put into by-pass (8).

Since there had been a drastic shift in the TDR as a function of nitrogen content beyond the 300 ppm level an intermediate concentration of 348 ppm was investigated. A TDR of 13 was produced by this concentration of nitrogen which was in agreement with the previous trend. A complete breakpoint temperature analysis was run on the 348 ppm nitrogen fuel and was compared

to undoped fuel. The nitrogen containing fuel produced a pressure drop failure at 254°C, and this failure was 25°C lower than the breakpoint temperature of the undoped fuel. This was only an approximation since the breakpoint temperature of the undoped fuel was greater than 279°C (10).

Attention was then shifted to identification of the nitrogen compounds in the acid extract. Some preliminary analytical work performed by NAPC and NRL showed the nitrogen compounds to be primarily substituted pyridines with alkyl substituents with two to nine carbons; quinolines with zero to four carbons and tetrahydroquinolines with two to four carbons. A thermal oxidation stability analysis was made on pure nitrogen compounds in a petroleum derived JP-5. The results showed that pyridine type compounds are innocuous at concentrations between 50 and 100 ppm. Pyridine compounds containing primary amine functional groups are deleterious to thermal oxidation stability. Pyrroles are also deleterious (11).

The next area of investigation was directed towards the evaluation of the storage stability of oil shale fuel containing low amounts of acid extractable nitrogen. The test employed was accelerated, subjecting fuels to 60° temperature for four weeks. The containers used in this test were 1.1 liter actinic glass jars. A one liter quantity of fuel was used. The containers were capped with aluminum foil to permit breathing during the storage period. Water was added at a concentration of 1.0 percent. The shale oil fuel samples were prepared by extraction with 1.10N HCl to remove the basic nitrogen, followed by silica gel percolation to remove the remaining nitrogen. The shale oil samples were then doped with the acid extracted nitrogen compounds to a concentration range of 8 to 125 ppm basic nitrogen. Some samples contained 25 ppm of an organic oxidation inhibitor, Dupont AO-22 (phenylene diamine), to determine if oxidation inhibition could be achieved during accelerated storage. A petroleum JP-5 with and without the inhibitor was incorporated in the study as a control (12). Thermal stability analyses of the samples before and after storage showed that small quantities of basic nitrogen, less than 20 ppm, caused the fuel to become unstable (13). However, the use of the inhibitor retarded this behavior (14). A high unacceptable level of peroxidation had also occurred during storage (15), however this was satisfactorily controlled by the inhibitor (16). There was some correlation observed between the peroxide content and the thermal oxidation stability of fuels containing low concentrations of nitrogen (17). This investigation also showed that a petroleum derived JP-5 with and without an oxidation inhibitor remained stable during this accelerated storage period.

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THERMAL OXIDATIVE STABILITY OF SYNTHETIC JET FUELS

NAVAIR 6.2 EXPLORATORY DEVELOPMENT PROGRAM

OBJECTIVE:

STUDY OF ORGANIC NITROGEN - EFFECTS OF CONCENTRATION LIMITS
AND STRUCTURE ON JP-5 FUEL THERMAL OXIDATION/STORAGE STABILITY

TEST APPARATUS:

- ASTM D-3241, JET FUEL THERMAL OXIDATION TESTER (JFTOT)

EVALUATION CRITERIA:

- TUBE DEPOSIT RATING (TDR) OF 17 OR GREATER CONSTITUTES A FAILURE
- OR A PRESSURE DROP IN EXCESS OF 25 MILLIMETERS ACROSS A FILTER DURING
2 1/2 HOURS

TEST NO. 1:

EFFECTS ON JFTOT BREAKPOINT TEMPERATURE OF OIL SHALE JP-5 WITH VARIOUS
CONCENTRATIONS OF ACID EXTRACTABLE ORGANIC NITROGEN - NONEXTRACTABLE
NITROGEN CONSTANT AT 116 PPM

RESULTS OF TEST NO. 1:

<u>ORGANIC NITROGEN, PPM IN FUEL</u>		<u>JFTOT BREAKPOINT TEMPERATURES, °C AT</u>	
<u>ACID EXTRACTABLE N</u>	<u>TOTAL N⁽¹⁾</u>	<u>HEATER TUBE</u>	<u>FILTER</u>
7	123	(254) (2)	279
50	166	251	(241)
97	213	243	(232)
838	954	244	(227)

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(1) NONEXTRACTABLE N CONSTANT 116 PPM.

(2) BRACKETED FIGURES INDICATE BREAKPOINT TEMPERATURE.

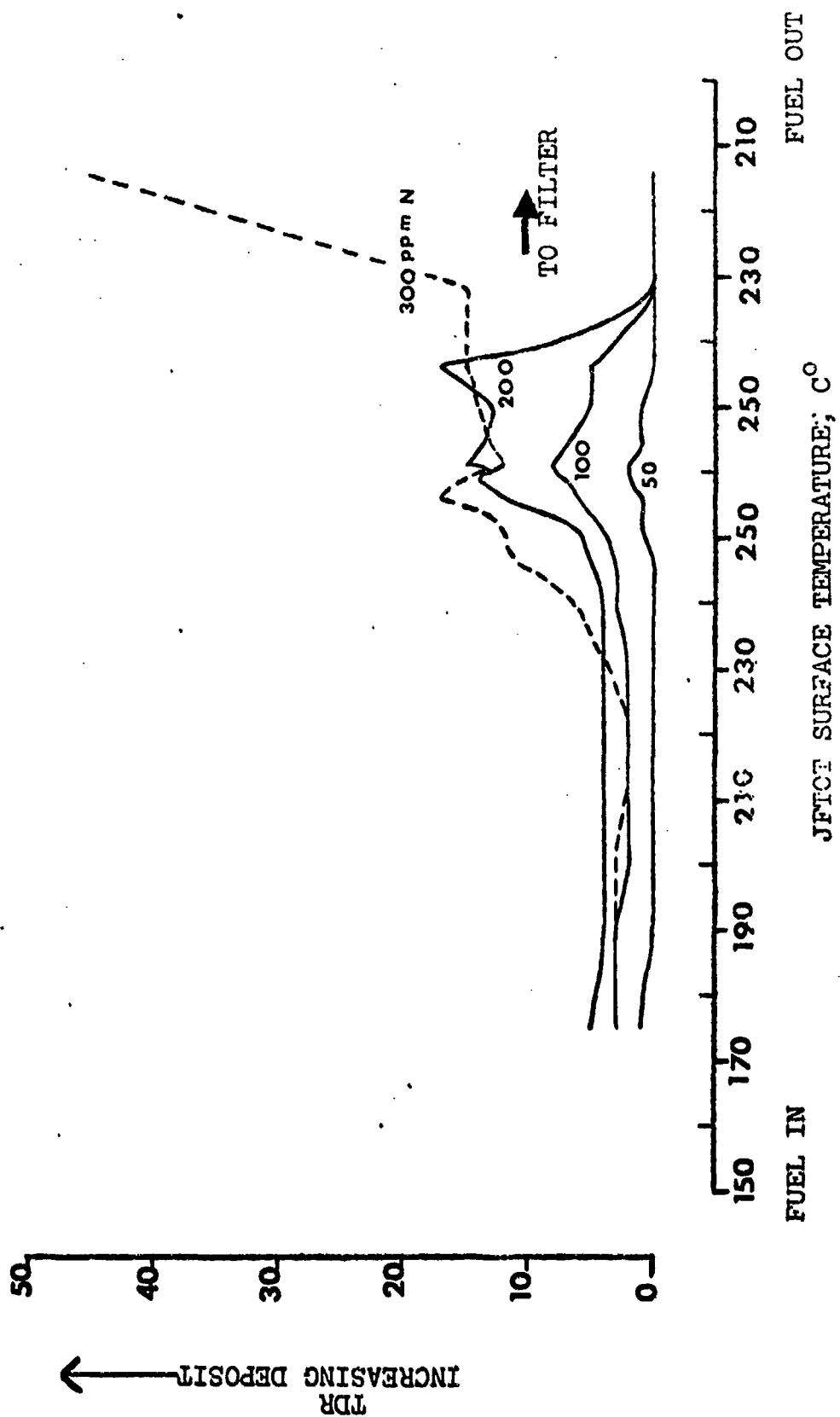
TEST NO. 2:

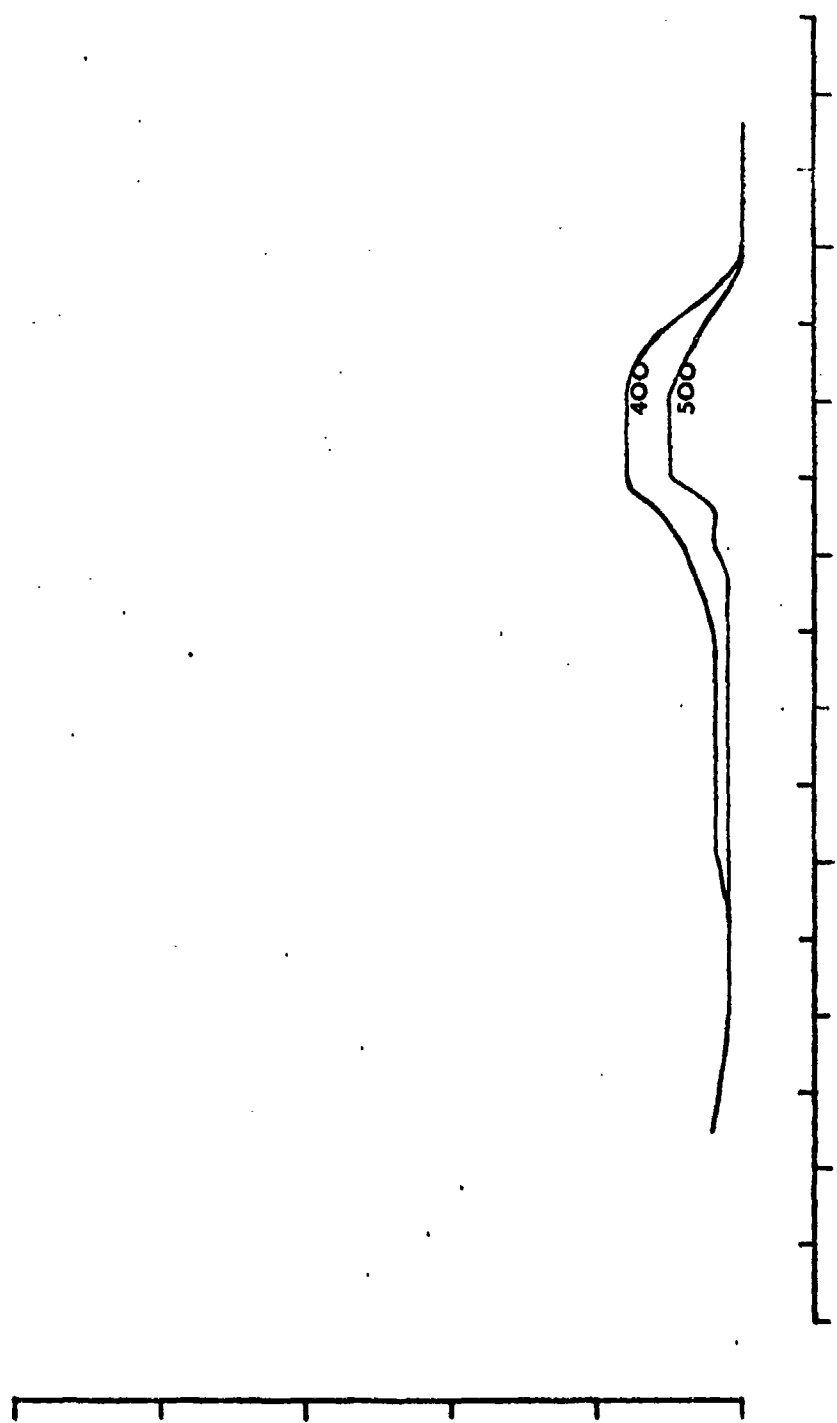
EFFECTS ON THERMAL OXIDATION STABILITY OF PETROLEUM DERIVED JP-5 WITH
VARIOUS CONCENTRATIONS OF ACID EXTRACTABLE ORGANIC NITROGEN - NONEXTRACTABLE
NITROGEN CONCENTRATION ZERO

RESULTS OF TEST NO. 2:

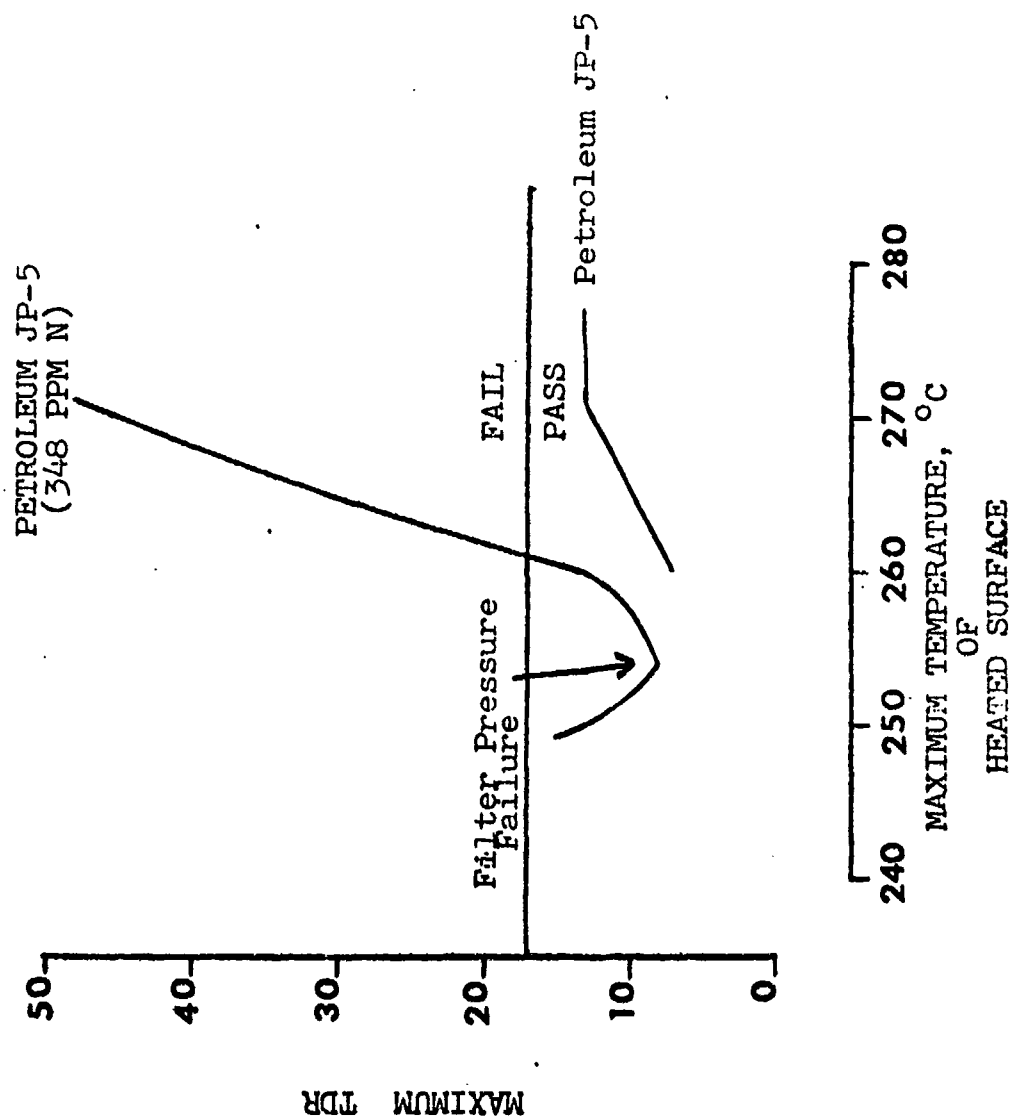
<u>NITROGEN CONCENTRATION, PPM</u>	<u>JFTOT RATING AT 260°C</u>	
	<u>MAXIMUM TDR</u>	<u>PRESSURE DROP</u>
50	2	BYPASS 124 MINUTES
100	8	BYPASS 120 MINUTES
200	17	BYPASS 120 MINUTES
300	45	BYPASS 88 MINUTES
400	8	BYPASS 86 MINUTES
500	5	BYPASS 84 MINUTES

EFFECT OF ORGANIC NITROGEN CONCENTRATION
ON FUEL THERMAL OXIDATION STABILITY





EFFECT OF ORGANIC NITROGEN ON BREAKPOINT TEMPERATURE OF JP-5



TEST NO. 3:

Compound Type	JFTOT Rating at 260°C		
	Concentration, ppm*	Maximum TDR	Pressure Drop, mm
4-t-butyl pyridine	28	6	8
4-t-butyl pyridine	56	1	20
2-t-butyl pyridine	49	10	1
5-ethyl-2-methyl pyridine	107	11	3
2,2-bipyridyl	42	5	0
2-amino-3-methyl pyridine	134	45	14
methyl 3-pyridyl ketone	78	14	10
4-benzyl pyridine	56	7	2
isopropyl quinoline	62	5	3
4-picoline	107	2	3
N,N-dimethyl aniline	82	6	5
Fractionated (160-175°C) Acid Extractable Nitrogen	116	7	0
Pyrrole	100	32	BYPASS
Acridine	70	4	0

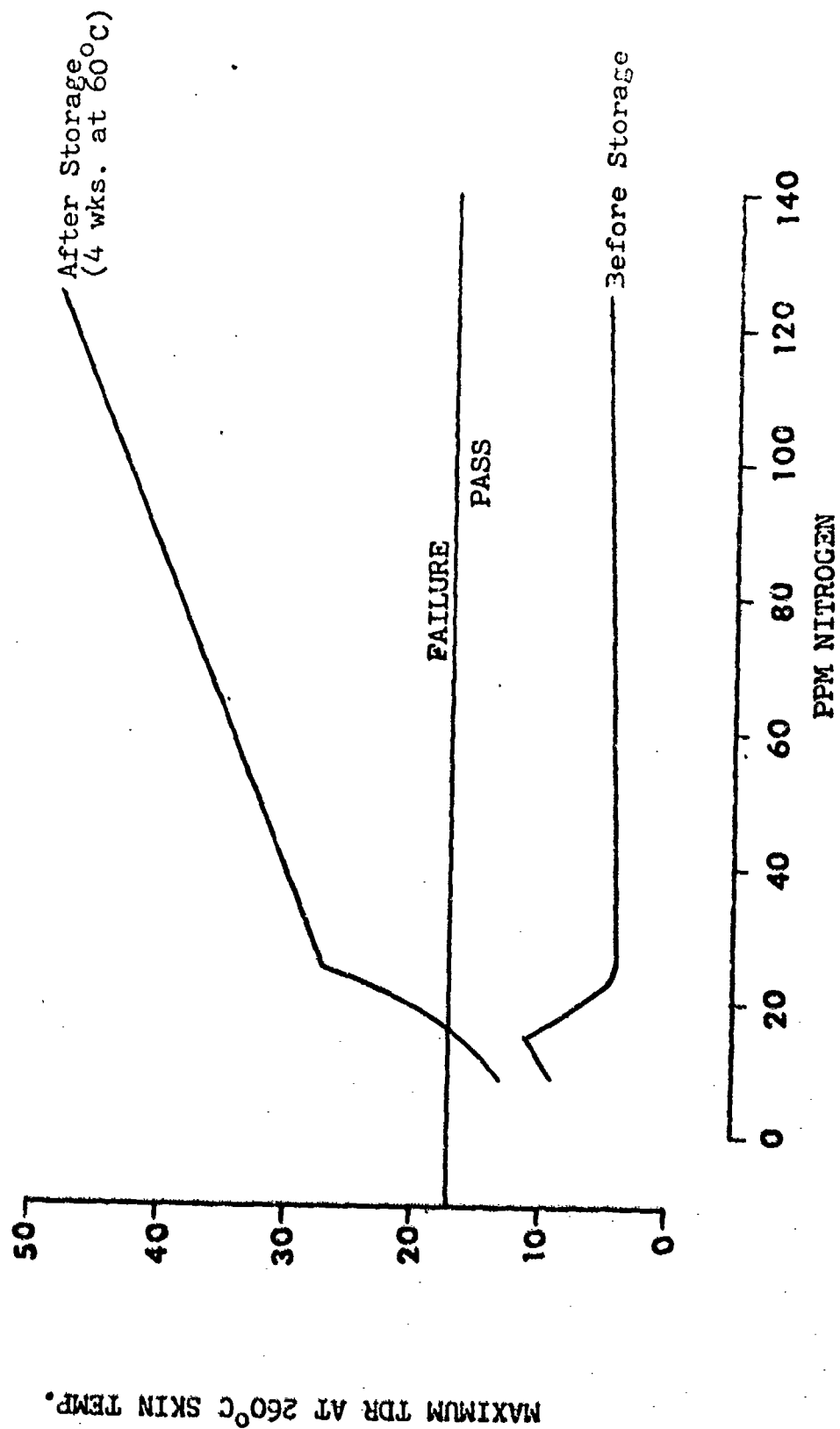
*Determined by perchloric acid titration.

TEST NO. 4:

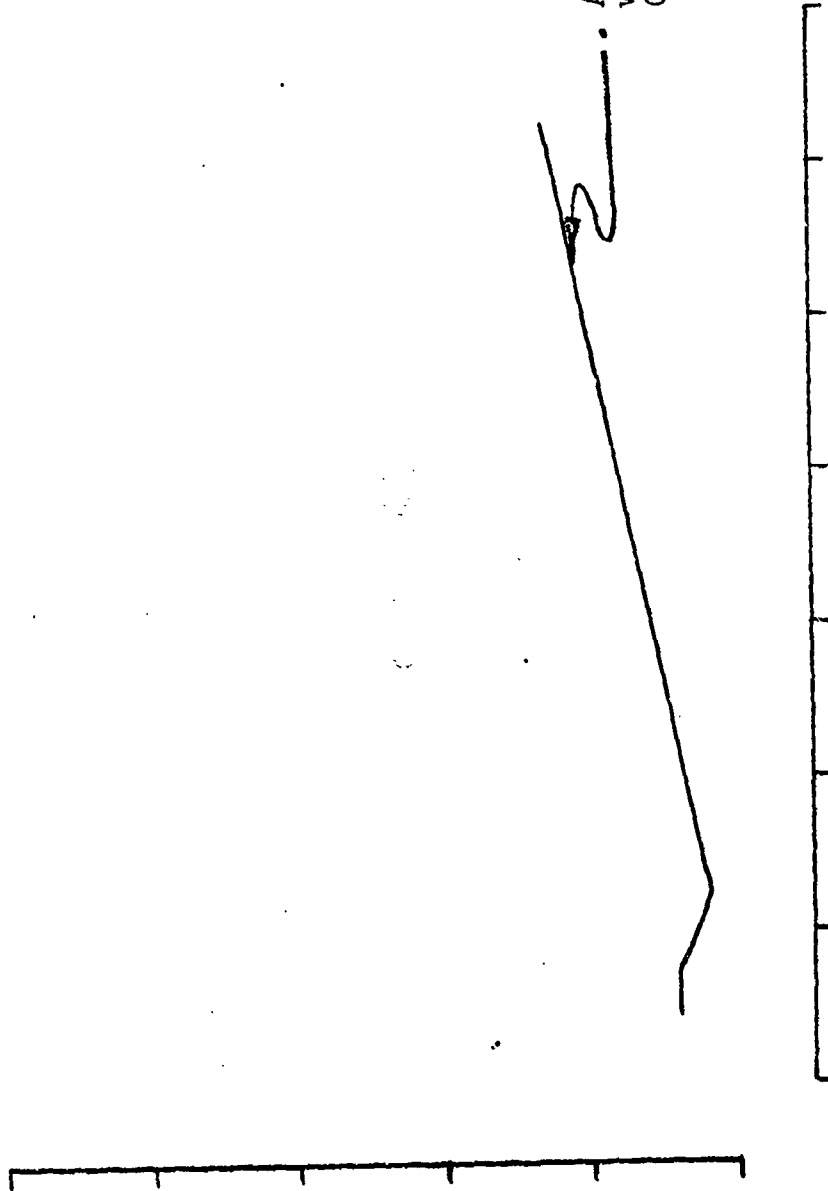
EFFECT OF ACID EXTRACTABLE ORGANIC NITROGEN ON ACCELERATED STORAGE OF
JP-5 DERIVED FROM OIL SHALE

- STORAGE CONDITIONS, 4 WEEKS AT 60°C
- FUELS WERE ACID EXTRACTED, FOLLOWED BY SILICA GEL TREATMENT
- ACID EXTRACTED ORGANIC NITROGEN ADDED TO NITROGEN FREE JP-5
DERIVED FROM OIL SHALE

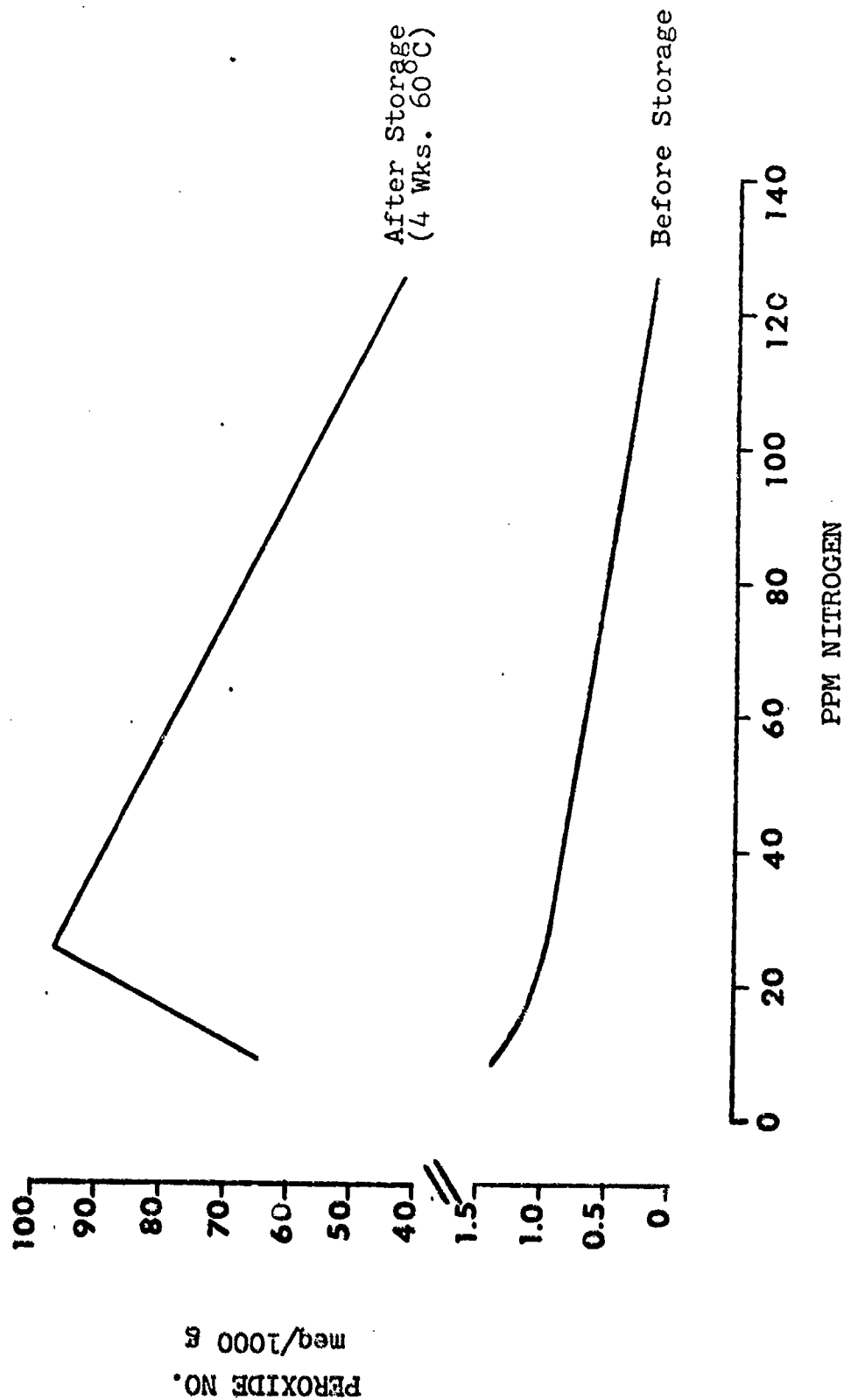
EFFECT OF ORGANIC NITROGEN ON FUEL
THERMAL OXIDATION/STORAGE STABILITY



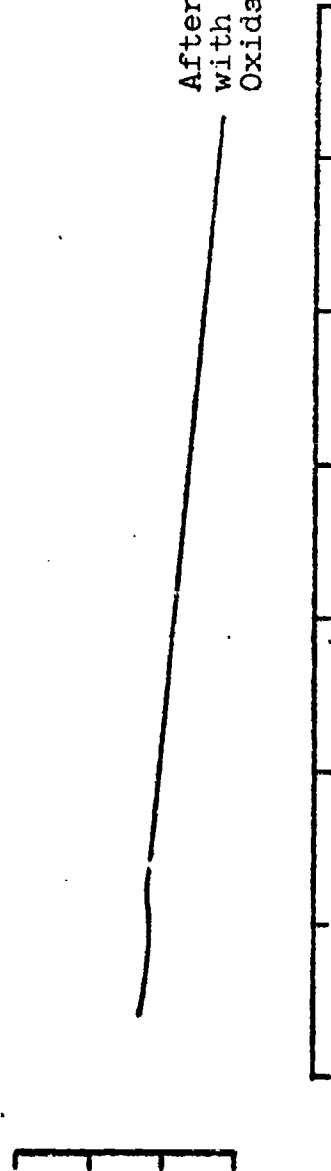
After Storage
with 25 PPM
Oxidation Inhibitor



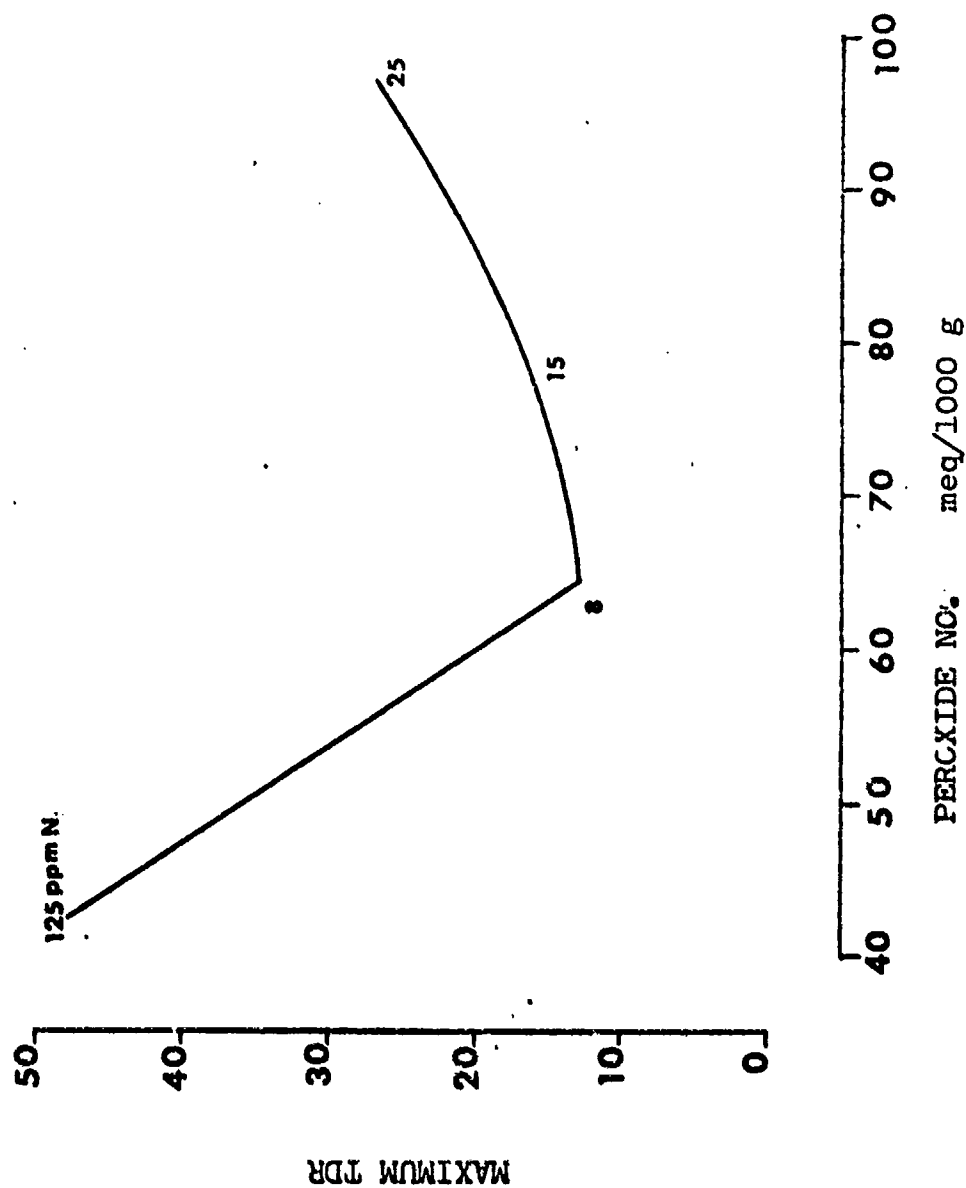
EFFECT OF ORGANIC NITROGEN ON PEROXIDE
FORMATION DURING ACCELERATED STORAGE



After Storage
with 25 PPM
Oxidation Inhibitor



RELATIONSHIP BETWEEN FUEL THERMAL OXIDATION STABILITY AND PEROXIDE CONTENT



STORAGE STABILITY AND NITROGEN CHEMISTRY

by: John W. Frankenfeld
William F. Taylor

Exxon Research and Engineering Company
Linden, New Jersey

Present petroleum derived jet fuels experience few problems resulting from nitrogen compounds (as attested to by the lack of a total nitrogen level fuel specification), since they presently contain little if any nitrogen (e.g., less than 5 ppm total N). However, synthetic crude oils, particularly as derived from shale rock, contain drastically higher levels of nitrogen. In addition, research has indicated that such nitrogen compounds are much harder to remove than other trace impurities, and it is highly probable that future alternate jet fuels will contain much higher nitrogen levels than present petroleum derived fuels. Studies have shown that certain trace nitrogen containing impurities promote sediment formation in fuels of the JP-5 type. This formation occurs at ambient temperature and is of sufficient magnitude to cause storage stability problems in such fuel. As a result, a study of the fundamental chemistry of sediment formation caused by nitrogen compounds is being carried out to provide a greater insight into the probable cause of sedimentation and provide a sound basis for future work aimed at establishing acceptable nitrogen levels in synfuels which optimize properties such as storage stability vs cost and availability considerations.

The major objectives of the present program were to determine the magnitude of the sedimentation problem, especially with respect to the number of nitrogen compound types which promote it, to study the effects of light, storage conditions and the presence of other non-hydrocarbon impurities and investigate the structure and mechanism of formation of the sediment.

In carrying out the program, a simplified model system with purified normal decane as the diluent was employed. Various nitrogen compounds were added alone or together with organic acids and phenols to determine their individual effects on sedimentation. Duplicate samples were stored under UV light and in total darkness. The sediments formed were removed periodically, weighed and analyzed for C, H, N and by infrared and mass spectral methods. The results obtained and conclusions reached are as follows:

- Nitrogen compounds of the types found in synthetic derived crude oils such as obtained from shale rock can cause the formation of significant quantities of sediment in relatively short times and thus pose a potentially serious problem in the storage stability area.

- The type of nitrogen compounds present in the fuel is very important as not all classes of nitrogen compounds are deleterious. Pyrrolic types, in particular, and some amines have been shown to be deleterious; however, many other types of nitrogen compounds are not.

● Structural effects among pyrrolic types appear to be important also as the sediment formation rate is very high with 2,5-dimethylpyrrole compared to the rate of sediment formation with other pyrrole derivatives.

● Light has a very strong catalytic effect which markedly increases the rate of sediment formation.

● The interaction of nitrogen compounds with other trace impurities can exert a strong, but complex effect on the rate of sediment formation. The presence of carboxylic acids strongly accelerates the rate of sediment formation, with this effect being most pronounced in the dark. In contrast, the presence of phenols reduces the rate of sediment formation. In addition, there are strong structural effects among phenolic types.

● The sediments have a definite structural character and with 2,5-dimethylpyrrole and indole appear to be a partially oxidized dimer, trimer, and/or tetramer of the parent nitrogen compound containing about 1.5 units of oxygen per unit of parent compound. More than one species may be present but all appear closely related.

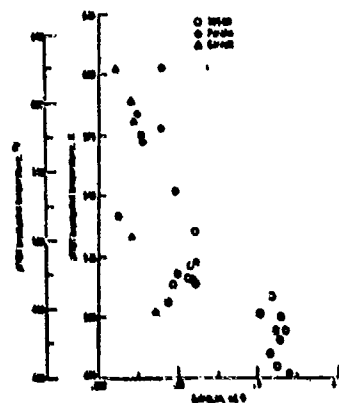
SLIDES

CHARACTERISTICS OF CRUDE OILS DERIVED FROM VARIOUS SOURCES

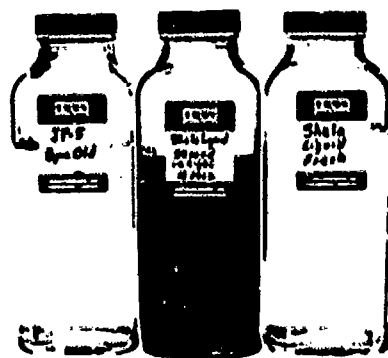
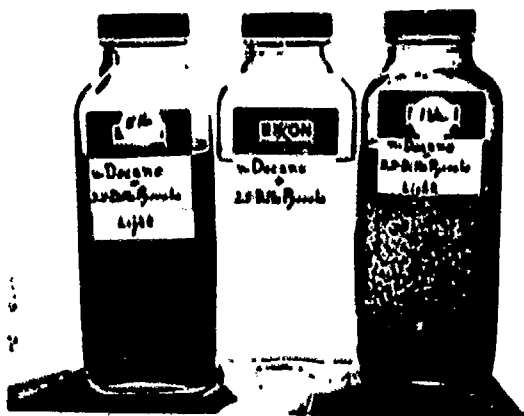
	<u>PETROLEUM</u>	<u>SHALE</u>	<u>COAL</u>
IN	.1-.5	1-3	.6-1
CO	0.3-3.0	6	7-13
SS	.6-6	.6-3	.3-2
SATURATES %	70-90	10-40	3-20
AROMATICS %	10-20	35-50	10-50
POLARS %	<1	1-3	50-80
OLEFINS	1-2	25-50	1-3

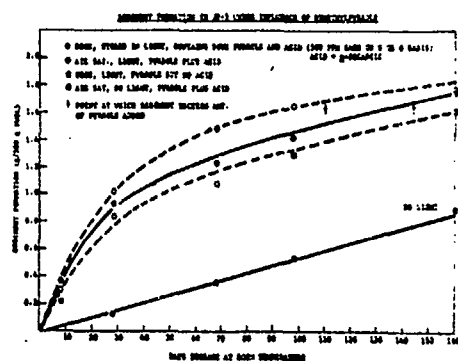
1

Variation of JFTOT Breakpoint Temperature
With Nitrogen Level After Hydrotreatment



2





5

NITROGEN COMPOUNDS FOUND IN SHALE OIL LIGHT DISTILLATE

TYPE	WT. % OF TOTAL N
ALKYLPIPERIDINES	42
ALKYLQUINOLINES	21
ALKYLPIPERIDINES AND INDOLES	19
CYCLOANILINES	3
ANILINES	2
WEAK AND NON-BASIC N	11

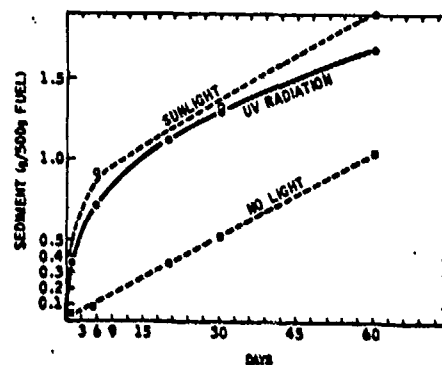
6

EFFECTS OF N COMPOUNDS ON SEDIMENT FORMATION IN N-DECANE (STORED IN LIGHT)

COMPOUND	SEDIMENT (g/500g DECANE)	
	10 DAYS	60 DAYS
2,3-DIMETHYLPIPERIDINE	1.13	1.69
INDOLE	.032	.043
CARBAZOLE	.019	.031
DIMETHYLANILINE	.004	.005
2-METHYLPIPERIDINE	.001	.001

7

EFFECTS OF UV RADIATION ON SEDIMENT FORMATION BY 2,3-DMP IN N-DECANE



8



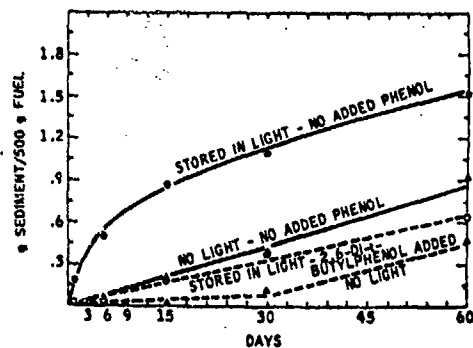
9

CATALYTIC EFFECTS OF ORGANIC ACIDS ON SEDIMENT FORMATION WITH DMP

ACID		SEDIMENT (g/500g DECANE)	
		10 DAYS	60 DAYS
NONE	LIGHT	.049	1.52
	DARK	.137	.040
DECAZOIC	LIGHT	1.25	1.64
	DARK	.497	1.50
CYCLOHEXANECARBOXYLIC	LIGHT	1.26	1.63
	DARK	.421	1.64

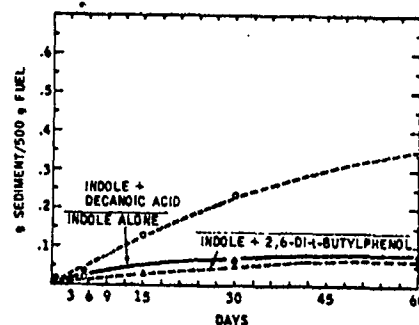
10

EFFECT OF DI-4-BUTYLPHENOL ON SEDIMENT FORMATION WITH 2,5-DIMETHYLPYRROLE IN DECANE



11

EFFECTS OF n-DECANOIC ACID AND 2,6-DI-4-BUTYLPHENOL ON SEDIMENT FORMATION WITH INDOLE IN n-DECANE - STORAGE IN PRESENCE OF UV LIGHT



12

EFFECTIVENESS OF VARIOUS PHENOLS IN RETARDING SEDIMENT FORMATION

PHENOL	FRACTION OF DMP ALONE			
	LIGHT		DARK	
	15 DAY	60 DAY	15 DAY	60 DAY
2,6-DITB	.20	.42	.20	.60
2,6-DITB-4-M	.31	.50	.16	.40
2-OM-3IP	.18	.54	.43	.83
2,4-DM	.79	.86	.93	1.2
2,4,6-TM	.63	.75	1.5	1.6
PHENOL	—	.87	—	.93

13

RELATIVE EFFECTIVENESS OF PHENOLS-SUBSTANCES VS. PETROLEUM

WITH DMP	PETROLEUM*
2,6-DITB	2,4,6-TM
2,6-DITB-4M	2,6-DITB-4M
2-OM-3IP	2,4-DM
2,4-DM	2,6-DITB
2,4,6-TM	PHENOL
PHENOL	

*MILON, 1942

INCREASING EFFECTIVENESS ↓

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SEDIMENTAL ANALYSIS OF SEDIMENTS FROM 2,5-DIMETHYLPYRROLE

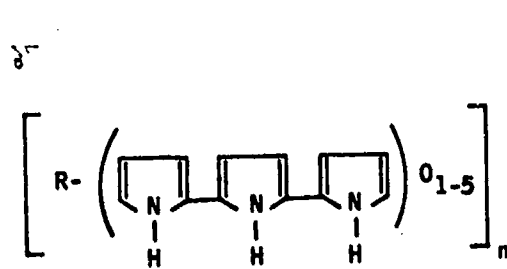
SEDIMENT	H.C.	H.H.	H.N.	H.O.
JP-5 (60 DAYS)	59.71	5.34	11.29	23.28
DECANE (5 DAYS)	62.28	5.33	11.86	20.53
JP-5 + C ₁₀ ACID	62.30	5.88	10.93	20.87
AFB. 11 SAMPLES	61.30	5.67	11.29	21.51
CALC. FOR C ₁₀ H ₁₈ N ₂ O ₂				
	C = 61.34	H = 5.94	N = 11.97	O = 20.31

15

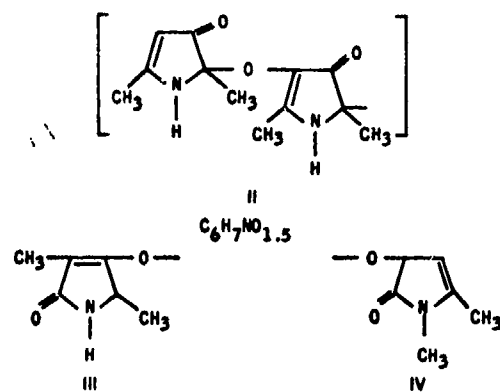
MAJOR IR BANDS IN SEDIMENT FROM 2,5-DIMETHYLPYRROLE

CM ⁻¹	SIGNIFICANCE
3300-3500 (s)	-NH or -OH
2970 (s) 1375 (s)	-CH ₃
2925 (v) 1450 (v)	LACK OF -CH ₂
1640 - 1670 (vs)	CONJ C=O OR AMIDE

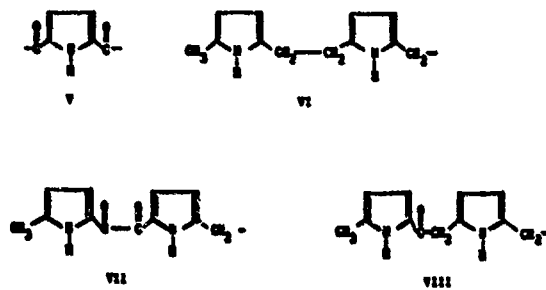
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17



18



19

SEDIMENT COMPOUND TYPES

SYNFUEL STORAGE AND THERMAL STABILITY

TEST RESULTS

by: Dennis W. Brinkman

U. S. Department of Energy
Bartlesville Energy Technology Center

Fuel stability research can be approached in many ways as shown in the variety of presentations at this workshop. One can look at pure compounds or simple mixtures; one can use a highly stable base fuel and spike it with compounds to be studied; or one can analyze actual fuels or crude cuts with the goal of correlating stability results with chemical and physical properties. All approaches produce worthwhile information, especially when intercorrelated with each other.

The program initiated by the Department of Energy at BETC about 18 months ago began with the last approach. We gathered what synfuels and relevant syncrude cuts we could find in sufficient quantities and performed extensive physical and chemical testing here and at Southwest Research Institute. A list of the samples characterized to date is presented in table 1. An example of the physical data is shown in table 2 for jet fuel samples. We feel very strongly that the properties of a material are much more important than a label, such as Shale Oil JP-5. The wide variety of materials that might fall under any one label precludes any meaningful conclusions. Table 3 presents results of 110° F storage stability tests. Most fuels look good until the 32 week sample, which correlates with at least two years of ambient storage. The high initial gum observed for the SASOL gasoline is being studied at this time. In another test, samples are sealed inside glass bottles and stored for 16 hours at 200° F. The ullage gases above the liquid are sampled at the end of this period for oxygen content, and then the fuel is analyzed for gum formation. These results are used to predict probable gum formation during 110° F storage. As can be seen in tables 4 and 5, the correlations work well for gasoline, the fuel for which the method was developed, but are not reliable for other fuels. Finally, table 6 presents JFTOT data for some of the samples, demonstrating thermal stability problems with the synfuels.

Present and future work in our program includes detailed analyses of the gums formed both in storage and thermal stability tests, as well as similar characterization of additional synfuels as they are made available. Expansion of our research into more basic investigations is being considered, along with an evaluation of various test methods used by the many labs measuring stability. We are also planning a detailed chromatographic characterization of each sample, which should provide valuable compositional data. When all is complete, we hope to publish a comprehensive report on which future processing decisions can be based.

SAMPLE
TABLE 1. - DESCRIPTION

SASOL GASOLINE

TAR SANDS NAPHTHA

TAR SANDS GAS OIL

TAR SANDS KEROSENE

COMMERCIAL REGULAR
GASOLINE - LEADED

COMMERCIAL UNLEADED
GASOLINE

PETROLEUM BASED JP-5

PARAHO SHALE OIL JP-5

TAR SANDS JP-5

COED COAL LIQUID JP-5

PARAHO SHALE OIL JET A #4

PARAHO SHALE OIL JET A #10

PARAHO SHALE OIL JET A #23

SRC-II NAPHTHA

SRC-II MID DISTILLATE

SRC-II HEAVY DISTILLATE

TABLE 2. - PHYSICAL AND CHEMICAL PROPERTIES OF JP-5 FUELS

Properties	Petroleum Based JP-5	Paraho Shale Oil JP-5	Tar Sands JP-5	COED Coal JP-5	Requirements of MIL-T-5624K for JP-5
Code No	AL-6300-T	AL-6326-T	AL-6354-T	AL-6355-T	
Acidity, Total, % KOH/g	0.01	0.02	0.04	0.08	0.015 max.
Aromatics, vol. %	12.9	23.2	20.1	15.6	25.0 max.
Olefins, vol. %	6.6	1.0	0.5	0.4	5.0 max.
Sulfur, Mercaptan, PPM	1.3	<1	<1	<1	10 max.
Sulfur, Total, wt %	0.027	0.015	<0.001	<0.001	0.40 max.
Distillation Temp., °C (°F)					
Initial Boiling Point	188(370)	173(344)	188(370)	181(358)	Report
1% recovered	195(383)	192(378)	202(396)	189(372)	205 (401) max
50% recovered	196(385)	199(390)	207(404)	192(378)	Report
90% recovered	202(395)	217(422)	221(429)	202(396)	Report
End point	227(440)	250(482)	250(482)	234(454)	Report
Distillation residue, %	263(505)	268(515)	278(532)	270(518)	290(554) max
Flash Point, °C (°F)	1.3	1.3	1.6	1.0	1.5 max.
Specific Gravity 15.6/15.6°C	0.7	0.2	0.4	0.5	1.5 max.
Gravity, API	61(141)	55(131)	59(138)	65(149)	60(140) min.
Freezing Point, °C (°F)	0.8109	0.8054	0.8289	0.8488	0.788-0.845
Viscosity 3 - 37.8°C (-30°F), cSt	43.0	44.2	39.2	35.2	36-48
Net heat of combustion, MJ/kg	-57(-71)	-53(-27)	-57(-71)	-68(-90)	-46(-51) max.
BTU/lb	8.25	-	12.77	8.90	NR*
Aniline Point, °C (°F)	42.594	42.810	43.131	42.480	42.6 min.
Aniline Gravity Product	18484	18405	18543	18263	18,300 min.
Corrosion, Copper Strip, Rating	61.0(141.8)	64.8(148.6)	59.7(139.5)	41.0(105.8)	NR
Existing Gum, mg/100 ml	6097	6568	5468	3724	4500 min.
Hydrogen, wt %	1A	1A	1A	1A	1B max.
Carbon, wt %	0.8	1.7	2.7	1.1	7 max
Oxygen, wt %	13.68	13.32	13.32	13.24	NR
Nitrogen, wt %	85.94	86.20	86.61	86.69	NR
	0.42	0.26	None	None	NR
	0.006	0.15	0.004	0.004	NR

* No Requirement

NOTE: Viscosity requirement at -20°C is 8.5 cSt max.

TABLE 3. - 43.3°C (110°F) STORAGE STABILITY TESTS
(mg/100 ml of fuel)

Description	Initial Total Gum	16 Weeks				32 Weeks			
		Inorg. Residue	Fuel Insol. Gum	Soluble Gum	Total Gum	Inorg. Residue	Fuel Insol. Gum	Soluble Gum	Total Gum
SASOL Gasoline	19.6	0	0.2	21.2	21.4	2.5	2.2	33.6	35.8
Tar Sands Naphtha	2.3	0.3	0.5	5.8	6.3	0.3	1.2	19.5	20.7
Commercial Regular Gasoline - Leaded	2.3	0.2	0.3	4.2	4.5	0.2	1.0	5.4	6.4
Commercial Unleaded Gasoline	4.0	0.1	0.4	4.0	4.4	0	1.4	9.5	10.9
Petroleum Based JP-5	0.3	0.02	0.7	0.5	1.2	0	0.9	1.7	2.6
Paraho Shale Oil JP-5	4.1	0.2	1.7	3.4	5.1	0	1.7	4.7	6.4
Tar Sands JP-5	1.6	0.1	1.0	7.3	8.3	0	1.0	25.0	26.0
COED Coal Liquid JP-5	2.0	0.2	0.9	2.6	3.5	0.3	2.9	25.0	27.9
Paraho Shale Oil Jet-A #4	2.5	0.04	0.4	4.4	4.8	0	0.1	116.4	116.5
Paraho Shale Oil Jet-A #23	2.7	0.04	0.4	1.8	2.2	0	0.2	1.6	1.8
Paraho Shale Oil Jet-A #10	3.1	0.04	0.2	1.6	1.8	0	0.3	1.8	2.1

TABLE 4. - ACCELERATED STORAGE TEST - 16 HOURS AT 93.3°C (200°F)

	AL-6789-G SASOL Gasoline	AL-6939-G Tar Sands Naphtha	AL-6951-G Regular Leaded Gasoline	AL-6976-G Unleaded Gasoline	AL-6400-T Petroleum JP-5	AL-6526-T Shale JP-5
Soluble gum, mg/100ml	37.6	13.6	9.8	10.0	0.6	3.6
Insoluble gum, mg/100ml	0.4	0.4	0.6	0.6	0.4	1.3
Total gum, mg/100ml	38.0	14.0	10.4	10.6	1.0	4.9
Inorganic residue, mg/100ml	0.1	0.1	1.3	0.1	0.1	0
Oxygen, % (in ullage)	20.9	21.0	18.7	18.3	20.2	19.9
Predicted gum after 32 weeks storage, mg/100ml *	21.6	3.6	11.6	13.0	1.8	5.7
Measured gum after 32 weeks storage, mg/100ml	35.8	20.7	6.4	10.9	2.6	6.4

*Calculated by method shown in Bulletin 660, Bureau of Mines (now BERC)
Swartz, F.G. and others, Storage Stability of Gasolines

TABLE 5. - ACCELERATED STORAGE TEST - 16 HOURS AT 93.3°C (200°F) cont.

	AL-6354-T Tar Sands JP-5	AL-6355-T COED JP-5	AL-7049-T Shale Jet A #4	AL-7050-T Shale Jet A #23	AL-7051-T Shale Jet A #10
Soluble gum, mg/100ml	2.0	1.8	1.8	0.6	1.2
Insoluble gum, mg/100ml	0.7	0.4	0.2	0.9	1.4
Total gum, mg/100ml	2.7	2.2	2.0	1.5	2.6
Inorganic residue, mg/100ml	0.1	0.1	0.2	0.1	0.1
Oxygen, % (in ullage)	20.2	13.7	20.6	20.8	20.2
Predicted gum after 32 weeks storage, mg/100ml*	3.2	3.9	3.2	2.5	3.8
Measured gum after 32 weeks storage, mg/100ml	26.0	27.9	116.5	1.8	2.1

*Calculated by method shown in Bulletin 660, Bureau of Mines (now BERC)
Swartz, F.G. and others, Storage Stability of Gasolines

TABLE 6. - JFTOT EVALUATIONS BY ASTM D 3241 METHOD

Sample Description	JFTOT Ratings				
	Visual	Spun Tube	Spot Deposit	ΔP , mm Hg/time, minutes	
SASOL gasoline	4	12	24	2/30	15/60 76/90 150/120 197/150
Tar sands naphtha	1	2.5	2.5	0/30	0/60 0/90 2/120 5/150
Commercial regular gasoline- leaded	1	1.5	6.0	145/30	145/60 148/90 148/120 148/150
Commercial unleaded	3	27	31	0/30	0/60 0/90 0/120 0/150
Petroleum based JP-5	1	4	6	1/30	1/60 1/90 2/120 2/150
Paraho shale oil JP-5	4	24.5	34.5	1/30	1/60 1/90 1/120 1.5/150
Tar sands JP-5	4	15	17	0/30	0/60 0.5/90 0.5/120 0.5/150
COED coal liquid JP-5	4	36.5	38	62/30	250/60
Paraho shale oil, Jet A (#4)	3	15	18	1/30	1/60 1/90 1/120 1/150
Paraho shale oil, Jet A (#23)	4	17	19	0.5/30	0.5/60 0.5/90 0.5/120 0.5/150
Paraho shale oil, Jet A (#10)	4	30	35	1/30	1/60 1/90 1/120 1/150

CRC LITERATURE SURVEY ON THERMAL OXIDATIVE
STABILITY OF JET FUELS

by: Robert Hazlett

Naval Research Laboratory

INTRODUCTION

Fuels for use in turbine powered aircraft require many specific properties to obtain desirable engine behavior and reliable fuel handling. One of the most critical of the jet fuel properties is that of thermal oxidative stability. This requirement became evident in the middle fifties and this subject still involves a major research effort.

The Coordinating Research Council Group on the Oxidation Stability of Gas Turbine Fuels has been a focal point for developing devices to measure thermal stability, to conduct cooperative testing, and to encourage research efforts. A Literature Survey Panel of the Group is putting together a critical literature survey at the present time. This survey, which emphasizes the knowledge developed since 1965, summarizes information on the topics listed on Slide 1. An expert on each topic has assimilated the available literature, written a critical survey, and abstracted the important references. The second drafts for these seven chapters have been completed and the literature survey should be published in 1979.

The meat of the survey is evident now, however, and the highlights are listed in Slide 2. It is noteworthy that qualitative agreement has been observed between laboratory testers and larger scale fuel simulators. Fuel injector nozzles are the most critical engine components with respect to thermal oxidation stability but the performance of fuel/oil heat exchangers and fuel controls can also be degraded by poor fuel. Minor constituents of fuels which contain oxygen, nitrogen, and sulfur are significant participants in fuel system deposit formation.

Slide 3 itemizes some of the R and D needs which stood out in the evaluation of the literature survey. Of particular note is the need to correlate small thermal stability tests with fuel behavior in engines. The rather sizeable gaps in temperature, time and flow character between the two test environments highlights the difficulty of establishing a meaningful correlation.

The chemistry of deposit formation needs additional study. Emphasis on hetero compound involvement is particularly crucial as synthetic fuels come into prominence. This statement is supported by NRL data in Slide 4 which shows the concentrating effect of nitrogen and sulfur for thermally formed deposits. The nitrogen concentration in the deposits is at least 10,000 that found in the fuel used in these stress tests.

Although the hetero compounds are present in trace amounts, sophisticated analytical instrumentation offers opportunities to examine the role of these compounds in thermal stability. For instance, a nitrogen specific detector for a gas chromatograph permits the estimation of nitrogen compounds in jet fuels even at total nitrogen contents of 100 ppm (Slide 5). Information from this type of analysis, when combined with gas chromatography/mass spectrometry can afford considerable information about the types of nitrogen compounds present in a fuel (Slide 6).

CRC LITERATURE SURVEY
JET FUEL THERMAL OXIDATION STABILITY

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- I. THE IMPORTANCE OF THERMAL OXIDATION STABILITY IN AIRCRAFT PROBLEMS
- II. SPECIFICATION AND NON-SPECIFICATION TEST DEVICES AND METHODS
- III. FUEL SYSTEM SIMULATORS
- IV. CHEMISTRY OF DEPOSIT FORMATION
- V. THE EFFECT OF DEOXYGENATION ON DEPOSIT FORMATION
- VI. CATALYSIS AND THE EFFECTS OF METALS ON DEPOSIT FORMATION
- VII. THE ROLE OF ADDITIVES IN DEPOSIT FORMATION

FIG. 1

HIGHLIGHTS

CRC LITERATURE SURVEY

- QUALITATIVE AGREEMENT BETWEEN SIMULATORS AND LABORATORY DEVICES
- CRITICAL ENGINE COMPONENTS - INJECTOR NOZZLES
 - F/O HEAT EXCHANGERS
 - FUEL CONTROLS
- REMOVAL OF OXYGEN USUALLY IMPROVES STABILITY
- COMPOUNDS CONTAINING O, N, AND S ATOMS ARE MAJOR DEPOSIT PRECURSORS
- CATALYSIS BY METALS, PARTICULARLY COPPER

R & D NEEDS

CRC LITERATURE SURVEY

- CORRELATE LABORATORY TESTS WITH ENGINE PERFORMANCE
- TEMPERATURE--TIME--FLOW CHARACTER-
- CHEMISTRY OF DEPOSIT FORMATION
- HETERO COMPOUND INVOLVEMENT
- DEOXYGENATION
- CATALYSIS
- ADDITIVES
- DEFINE THERMAL OXIDATION STABILITY OF SYNTHETIC AND BROAD SPEC. JET FUELS

**NITROGEN AND SULFUR
CONCENTRATIONS IN JET FUEL DEPOSITS**

FUEL SAMPLE	NITROGEN			SULFUR		
	IN FUEL*	IN DEPOSIT*	CONCEN. FACTOR	IN FUEL*	IN DEPOSIT*	CONCEN. FACTOR
AFFB-8	0.000063	2.1	33,000	0.019	1.6	82
9	0.000089	1.2	13,000	0.066	8.0	120
10	< 0.00001	3.0	> 300,000	0.014	1.2	88
11	< 0.00001	0.4	> 40,000	0.0003	0.24	970
12	0.000042	0.95	23,000	0.0003	0.74	2500
16	0.00014	1.3	10,000	0.019	1.0	54

* PERCENT BY WT.

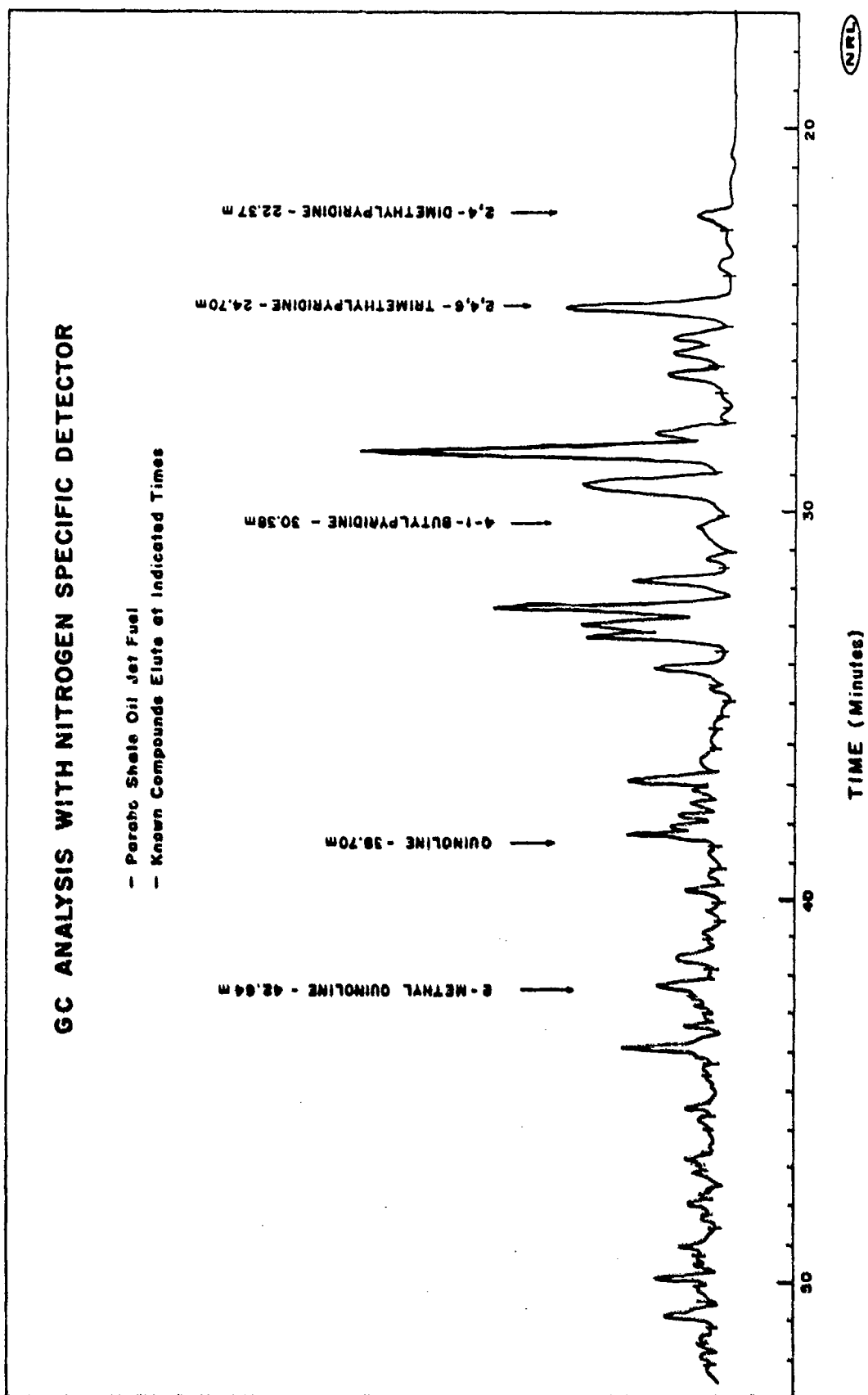


FIG. 5

TABLE II
Nitrogen Compounds in Shale A Jet Fuel*

	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Pyridines	-	-	+	++	+++	++++	+++	++	++	+	-
Quinolines	+	++	++	++	++	-	-	-	-	-	-
Tetrahydroquinolines	-	-	+	+	+	-	-	-	-	-	-
Pyrroles	-	++	++	-	-	-	-	-	-	-	-
Indoles	-	-	++	++	++	++	-	-	-	-	-

* - By GC-MS analysis.

COMBUSTION EXPERIMENTS WITH SYNTHETIC
JET FUELS

by: David Naegeli

Southwest Research Institute

COMBUSTION EXPERIMENTS WITH SYNTHETIC JET FUELS

Due to uncertainties in the production and supply of petroleum products, the U.S. Navy is considering two problems in obtaining adequate supplies of jet fuels:

- a. Shortages of acceptable products which may exist either worldwide or in specific areas, and
- b. The necessity or expediency, in certain cases, to use nonaviation fuels for aircraft.

The fuel specifications could be broadened, thus increasing the availability of fuels that are acceptable, or non-petroleum crudes could be used as refinery feed stock. However, the conflict in these approaches lies in the fact that fuel specifications are established to eliminate combustion and handling problems and assure an adequate supply of fuel. Engines now in production or under development were designed for satisfactory performance and life on the current specifications for petroleum base fuels; many of these engines may not be able to handle the stress implied by a broadened fuel specification, e.g., higher liner temperatures or lower rates of fuel vaporization. In many cases, the specific details of relating these problems to fuel chemistry have not been conducted; thus, the current specifications may not cover these same problems for syncrude fuels of different composition.

Among the fuel properties of greatest concern to turbine engine combustion are the composition, the end point of the distillation curve and the viscosity. The first property is generally associated with flame radiation and exhaust smoke; the latter two affect atomization and vaporization and, therefore, combustion efficiency. Fuel-bound nitrogen is one new fuel property which has emerged from the use of syncrude fuels because of the additional NO_x found in the exhaust.

APPROACH

A Phillips 2-inch diameter cylindrical research combustor designed for high temperatures and pressures was operated over a matrix of conditions involving:

- a. Burner inlet pressure, BIP = 2, 5, 10 and 15 atm.
- b. Burner inlet temperature, BIT = 532, 812, and 1034°K.
- c. Fuel-air ratio (heat input rate), H = 212, 424, and 848 KJ/kg of air.
- d. Reference velocity (turbulence and residence time) v = 22, 44 and 66 m/sec.

Flame radiation, exhaust smoke and gaseous emissions including CO_2 , CO, NO, NO_2 , O_2 and unburned hydrocarbons were measured.

Six petroleum-based JP-5 blends and three JP-5 syncrudes shown in Slide 1 were used to address the following questions:

1. How will flame radiation and smoke be affected by increasing the allowable aromatic content?
2. How are flame radiation and smoke affected by the types of aromatics that are present, i.e., single, double, or triple ring?
3. How will combustion be affected by raising the end point of the distillation curve?
4. How are gaseous emissions affected by these changes in fuel properties?
5. How do the combustor performance/fuel property correlations for syncrude fuels compare with the correlations for conventional petroleum-based fuels?

RESULTS

Slide 2 shows correlations of flame radiation with hydrogen content, ring carbon and aromatic content. Hydrogen content was found to be the best correlating parameter for both petroleum base and syncrude fuels. Similarly, hydrogen content was also the best correlating parameter for exhaust smoke.

Slide 3 shows that flame radiation is increased by increasing pressure, inlet temperature, and fuel/air ratio and is reduced by increasing reference velocity. In the case of exhaust smoke, it is increased by increasing pressure and fuel/air ratio and reduced by increasing reference velocity and inlet temperature. The slopes, dR/dH and dS/dH , of these curves are defined as the fuel sensitivities.

Slide 4 shows how fuel sensitivity of flame radiation increases as the level of flame radiation is increased by changing burner inlet conditions. At the highest radiation levels, the fuel sensitivity decreases because the flame emissivity appears to be approaching unity.

Slide 5 shows that the fuel sensitivity to exhaust smoke increases as the level of exhaust smoke is increased by changing burner inlet conditions.

Slides 6 & 7 list the conclusions. These conclusions are based largely on the flame radiation and exhaust smoke measurements. The emissions of CO and unburned hydrocarbons were very low (i.e., high combustion efficiencies, >99%) and there were no detectable differences between the fuels tested. NO_x levels were also essentially the same for all fuels except the syncrude from oil shale which contained fuel bound nitrogen.

RECOMMENDATIONS

1. The correlating parameter, hydrogen content or H/C ratio, should be tested further by measuring flame radiation and exhaust smoke for a series of fuels with equal hydrogen contents, but otherwise, large variations in composition.
2. It is generally accepted that carbon formation in flames is determined by fuel composition. Will a correlating parameter such as H/C ratio also describe non-specific fuels such as alcohols, alcohol/petroleum fuel blends and water/fuel emulsions? Measurements of flame radiation and soot formation from these fuels in a research combustor may give more insight into the mechanism of soot formation in spray combustion.
3. It has been argued that emulsified fuels yield less exhaust smoke because micro-explosions of fuel droplets cause secondary atomization. This theory should be tested in a high pressure research combustor. It has been suggested in a paper by C.K. Law that the probability of the micro-explosion event increases as the pressure is increased. An emulsified fuel should then yield relatively less exhaust smoke than a neat fuel as pressure is increased.

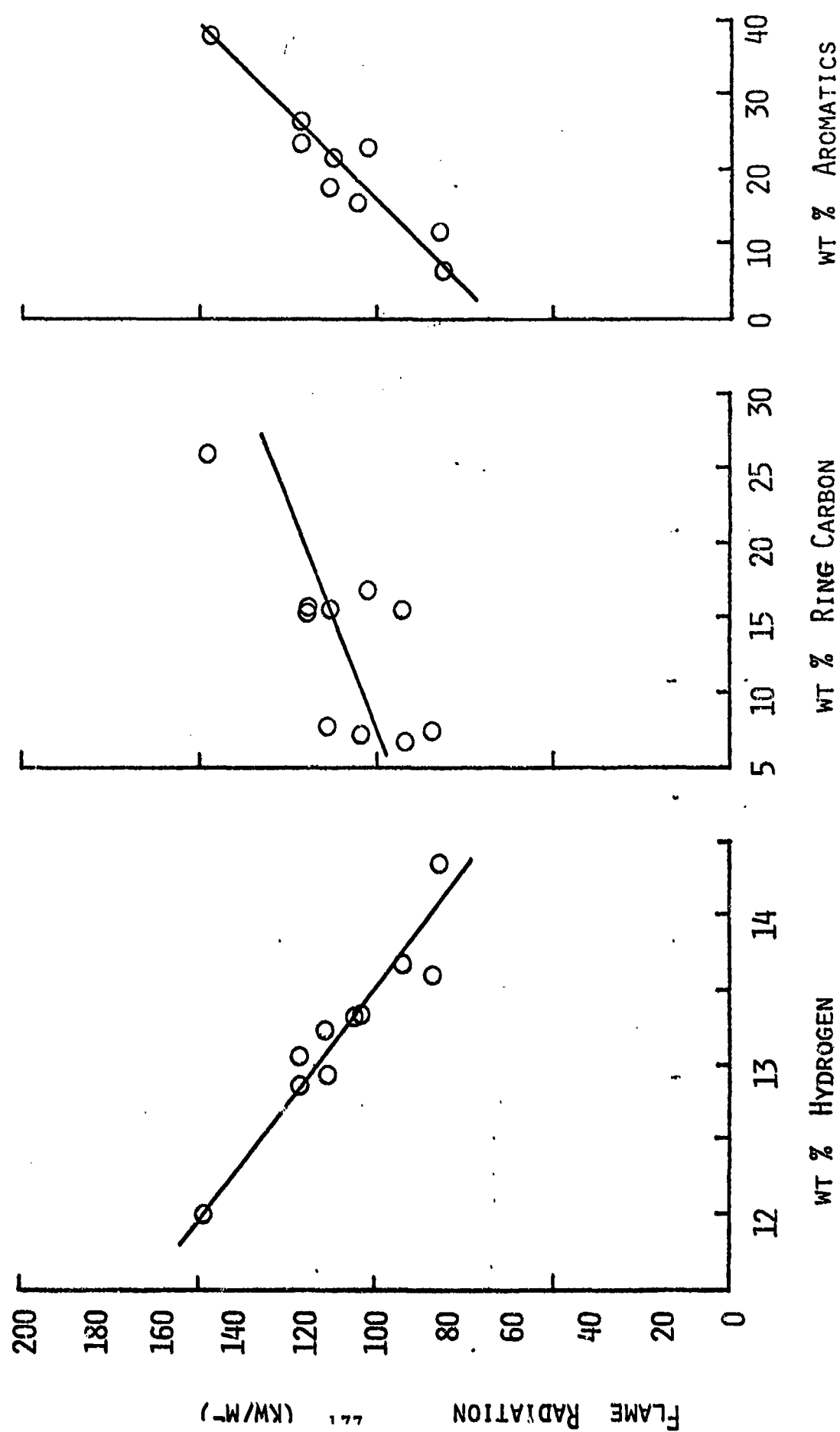
A P P R O A C H

TEST FUELS

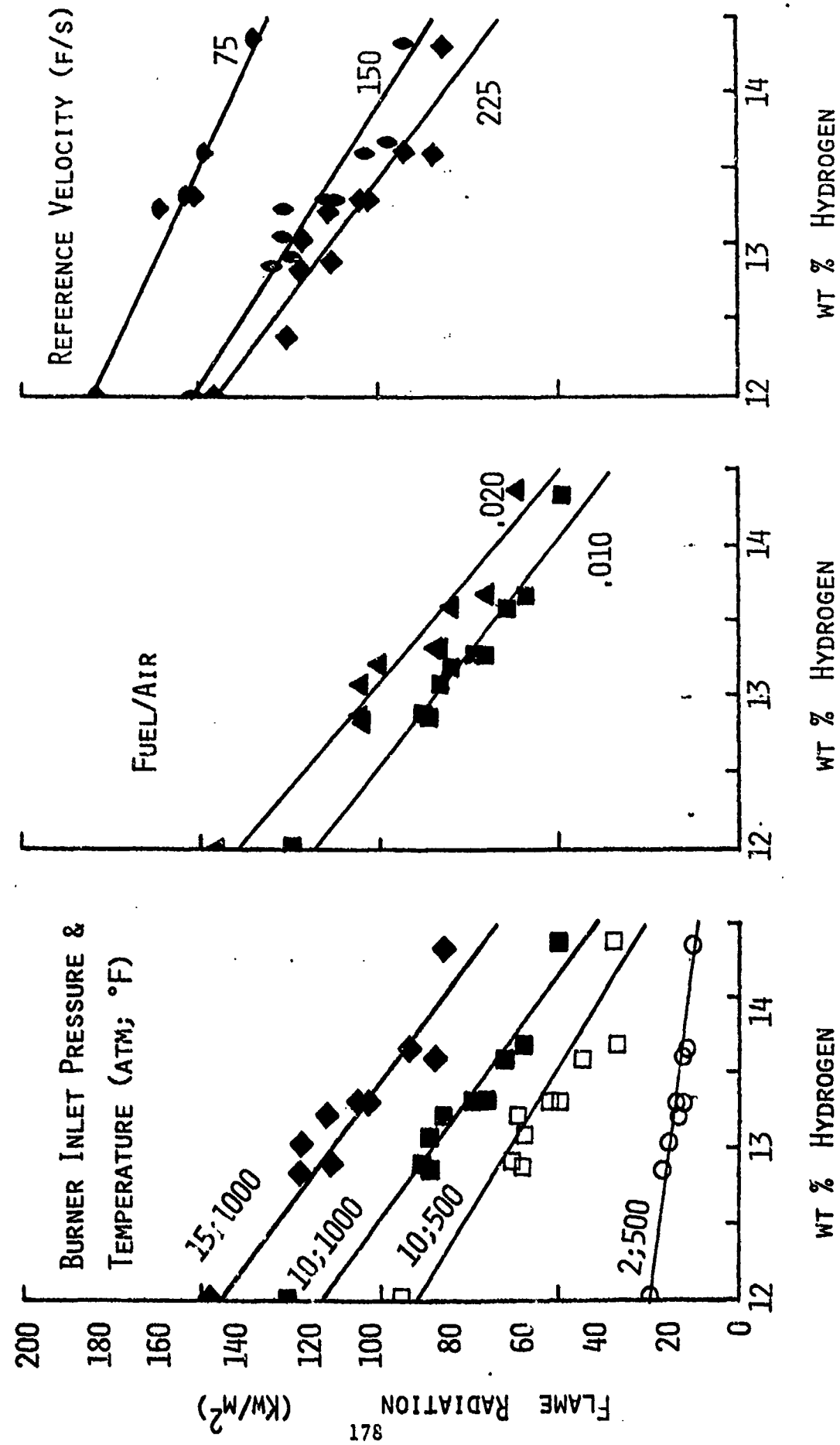
1. JP-5 BASE FUEL
2. SMOKE POINT REDUCED TO 16MM WITH POLYCYCLIC AROMATICS
3. SMOKE POINT REDUCED TO 16MM WITH MONOCYCLIC AROMATICS
4. AROMATICS INCREASED TO 40%
5. AROMATICS INCREASED TO 25%
6. END POINT RAISED TO 580°F
7. JP-5 - OIL SHALE
8. JP-5 - COAL
9. JP-5 - TAR SANDS
10. JET-A

NOTE: ADDITIVES WERE BLENDS TYPICAL OF JP-5 BOILING RANGE RATHER THAN
SINGLE COMPOUNDS.

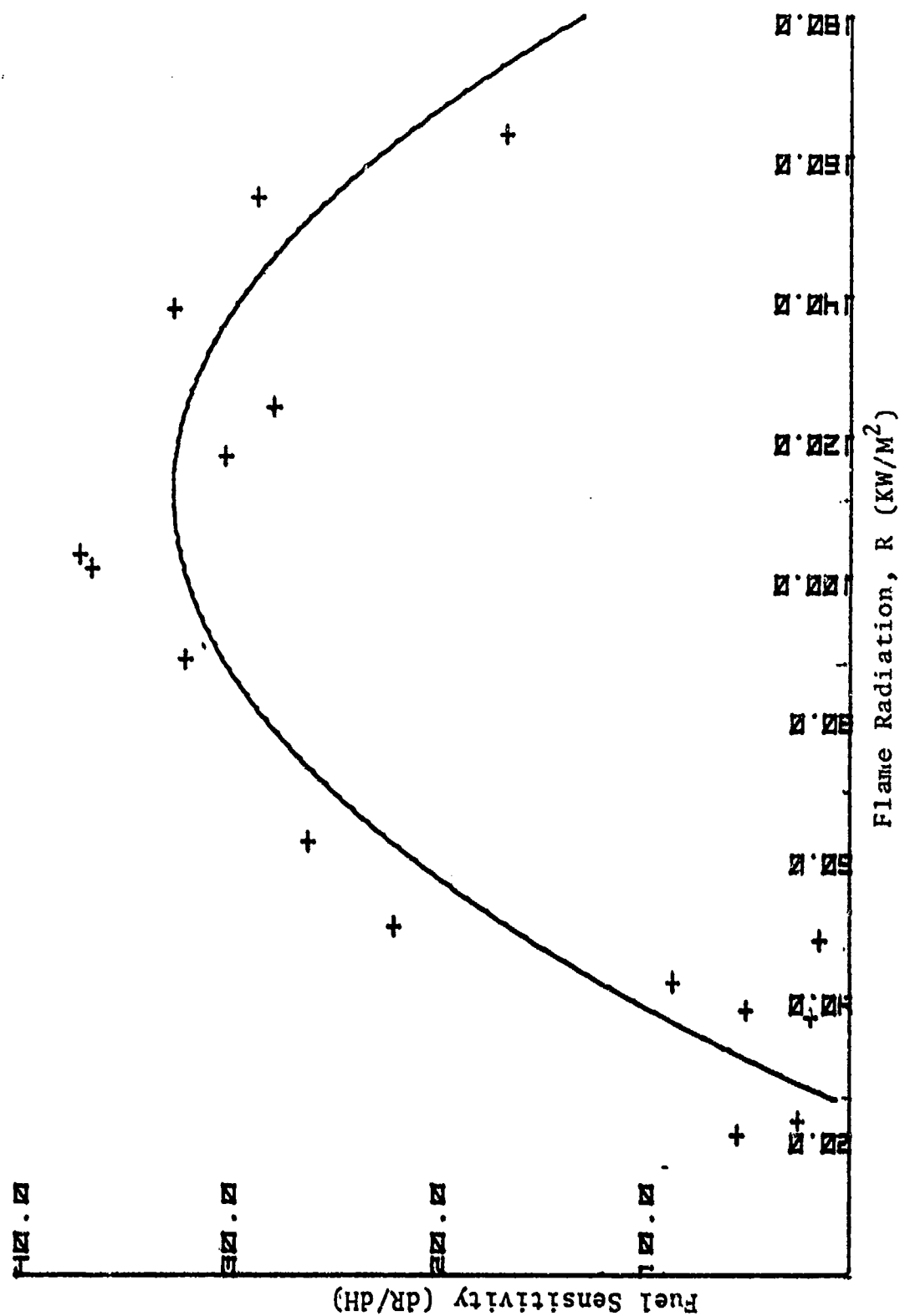
CORRELATIONS OF FLAME RADIATION WITH FUEL PROPERTIES



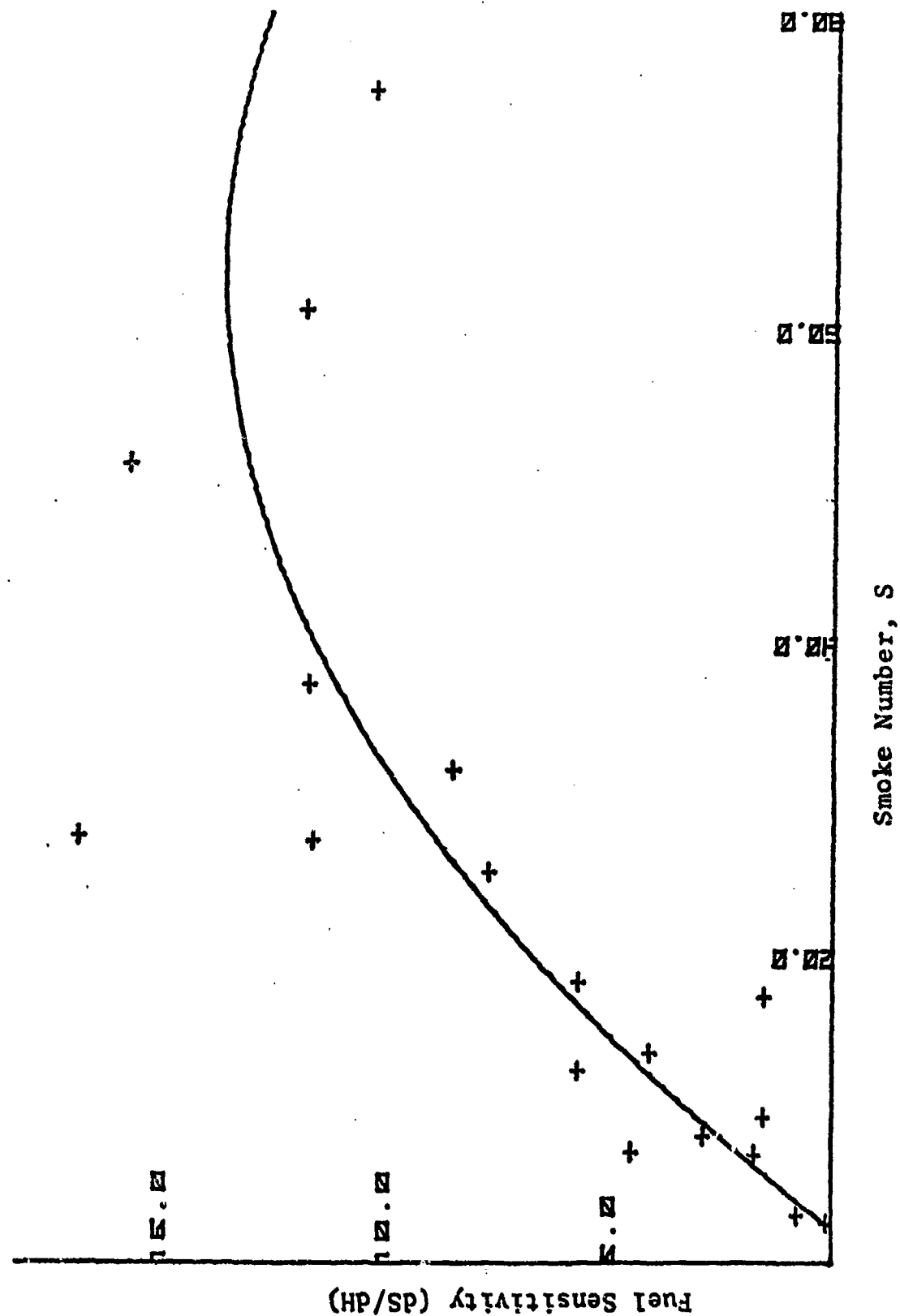
EFFECTS OF COMBUSTOR OPERATING CONDITIONS ON FLAME RADIATION



FUEL SENSITIVITY OF FLAME RADIATION



FUEL SENSITIVITY OF EXHAUST SMOKE



C O N C L U S I O N S

- HYDROGEN CONTENT WAS THE MOST EFFECTIVE PARAMETER FOR CORRELATING FLAME RADIATION AND SMOKE TO FUEL PROPERTIES. SOME FURTHER SENSITIVITIES TO HYDROCARBON STRUCTURE ARE APPARENT, BUT THE DATA BASE IS TOO SMALL TO DRAW CONCLUSIONS.
- WITH REGARD TO BURNING QUALITY, SOOT FORMATION, THE SYNCRUDE FUELS WERE SIMILAR TO PETROLEUM WHEN CORRELATED WITH HYDROGEN CONTENT.
- FUEL SENSITIVITIES OF FLAME RADIATION AND SMOKE ARE DETERMINED BY THE LEVEL OF RADIATION AND SMOKE.
- CLEAN BURNING COMBUSTORS SHOULD HAVE LOWER SENSITIVITY TO FUEL PROPERTIES FOR FLAME RADIATION AND SMOKE.

- INCREASING END POINT TO 580°F DOES NOT SIGNIFICANTLY AFFECT COMBUSTION EFFICIENCY UNDER CONDITIONS OF HIGH COMBUSTION EFFICIENCY.
- NO INDICATION THAT INCREASING END POINT TO 580°F AFFECTS SMOKE OR FLAME RADIATION (SOOT FORMING REACTIONS ARE GAS PHASE, NOT LIQUID-PHASE PYROLYSIS).
- HIGHER INLET AIR TEMPERATURES REDUCE THE CONVERSION EFFICIENCY OF FUEL BOUND NITROGEN TO NO_x .

AIR FORCE COMBUSTION STUDIES AND PLANS

by: Charles Martell

Wright Patterson Air Force Base

Cheap, high quality petroleum is rapidly becoming a thing of the past. The Department of Defense and other aviation turbine fuel users can anticipate higher fuel costs, reduced fuel availability, and lower quality fuels. These problems will become especially acute with the world-wide petroleum shortage forecast for the late 1980's.

The Air Force is pursuing two approaches as partial solutions to the petroleum shortage. One approach is to broaden aviation turbine fuel specifications to increase fuel availability and to help avoid some future cost increases. The second approach is to assure that fuels from alternative domestic hydrocarbon resources, i.e. coal and oil shale, can be utilized as they become available. Previous studies have established that oil shale is the most promising source of jet fuels from CONUS non-petroleum fossil fuel resources, and emphasis should be placed on the production of aviation turbine fuel from oil shale.

Broadened specification fuels are anticipated to have higher end points and higher freezing points and a lower hydrogen content. The combustion of these fuels will result in increased smoke and particulates, higher combustion liner temperatures, and degraded starting and altitude relight performance. Fuels derived from oil shale will have a high fuel-bound nitrogen content unless the nitrogen is removed through expensive processing. High fuel-bound nitrogen content results in increased nitrogen oxides in the exhaust and severe fuel stability problems.

Existing aircraft and engines will be limited in their ability to use broadened specification fuels. Increased exhaust smoke, degraded starting and high altitude relight, and decreased combustor life are anticipated. Possible actions include the retrofit of improved combustors, the rapid phase-out of older aircraft and engines, the use of broadened specification fuels only for newer systems while retaining JP-4 for the older systems, and the acceptance of decreased performance and higher maintenance costs for lower fuel costs and increased availability.

New systems can use improved combustors and combustion technology to handle broadened specification fuels. For example, premixed, prevaporized combustors with a lean primary zone and with variable geometry can handle a wide range of fuels while controlling smoke, nitrogen oxides, and other exhaust emissions. Improved combustor cooling techniques (and the reduction of particulate formation) will control combustor overheating problems. A small pilot burner may be necessary to provide adequate low temperature starting, high altitude relight, and combustion stability, however. This technology is available at this time. Some of the newer engines already use some of these advanced techniques and have demonstrated a significantly greater tolerance for broadened specification fuels than older engines.

New novel combustion techniques hold the promise for further improvements in the ability to use broadened specification fuels. Catalytic combustors can operate stably at very low fuel/air ratios with essentially 100% combustion efficiency. Fuel reforming, through partial oxidation, can convert any liquid hydrocarbon fuel into gaseous hydrogen and carbon monoxide, ideal fuels from the combustor designers viewpoint. Microwaves, ultraviolet light, and electric fields may be used to enhance combustion and may lead to the development of entirely new combustion concepts with further improvements in the ability to burn a wide range of fuels.

The Air Force Office of Scientific Research (AFOSR), the Air Force Aero Propulsion Laboratory (AFAPL), and the Civil and Environmental Engineering Development Office (CEEDO) at Tyndall AFB sponsor combustion and combustion related research programs. AFOSR sponsors a broad range of combustion research programs. For specific information about these programs contact Dr. B. T. Wolfson, AFOSR, Bolling AFB, Washington DC, telephone AC 202, 767-4937. The CEEDO programs are primarily directed towards environmental considerations. The AFAPL programs include ramjet, turbine, magnetohydrodynamic and fuel related R & D. The fuel related programs of the AFAPL are the ones primarily concerned with the combustion of fuels from alternate sources and are the ones that I will discuss.

The AFAPL Fuels and Lubrication Division has an active basic research program that includes the following:

Hydrocarbon Pyrolysis Study - Jointly funded by the DOE and AFAPL, this contractual program with the Exxon Research and Engineering Company is attempting to formulate a quasi-global fuel combustion model that takes into account variations in fuel type and composition.

Photochemically Assisted Combustion - Jointly funded by the AFOSR and AFAPL, this contractual program is also with Exxon Research and Engineering Company. The use of ultraviolet radiation to initiate, stabilize, and augment combustion is being studied. A wide range of potential applications are possible including laser ignitors, no-pressure drop flameholders, and increased reaction rates within conventional combustors.

Combustion Modeling and Advanced Combustion Diagnostics Study - This is a combined in-house and contractual study involving the new combustion tunnel at the AFAPL. Purdue University will help design experiments and will also use the experimental results to validate and refine combustion models. A wide variety of combustion diagnostics including LARS, CARS, LDV, thermocouples, and probes will be used to make measurements in the combustion tunnel and the results will be compared to establish the validity of the newer methods (and some of the older ones). These measurements will be given to Purdue University for the combustion model work, above. Contractors involved include: The University of Dayton Research Institute, Systems Research Laboratory, Centro Company, and Purdue University. This program involves all Divisions of the AFAPL.

Most of the Fuels and Lubrication Division's exploratory development (6.2) programs, and the proposed advanced development (6.3) programs to begin in FY79, pertain to the combustion performance of broadened specification fuels and fuels derived from oil shale and other non-petroleum sources. Various in-house and contractual programs are underway or planned to determine the fuel characteristics that will result in adequate system performance with the minimum life cycle costs. Essentially, fuel processing costs will be traded off against aircraft and engine development and maintenance costs.

Considerable data have already been obtained in-house using a T-56 combustor and a wide range of fuel properties. Detroit Diesel Allison has recently completed a test of a new high Mach combustor using experimental fuels varying in hydrogen content, end point, and fuel type (JP-4 vs JP-8). General Electric Company is currently under contract to test the J-79 low-pressure, can type combustor and the F-101 high pressure, annular type combustor using 12 experimental fuels. A contract change is underway to add a thirteenth fuel, number two Diesel fuel. Procurement action is underway to contract for a similar tests program using a high pressure, can type combustor.

These programs will determine the effects of fuel characteristics on combustor performance and predicted combustor life. Based on these and similar programs, an interim, broadened fuel specification will be prepared in the 1981-82 time period.

The Advanced Development program will continue fuel tests using fuels selected on the basis of the current programs and also including candidate fuels derived from oil shale and other fossil sources. These tests will progress from part-scale combustor tests to full scale engine tests. These programs will provide the necessary information on fuel combustion effects for the trade-off study. Ultimately, flight tests will be conducted prior to the publication of the final, broadened fuel specification.

Concurrently with the combustion tests, studies will be conducted to provide the necessary fuel processing cost data needed for the trade-off study.

Dr. Hazlett also asked that I address the relationship between the elemental hydrogen content of a fuel and its combustion characteristics. For the older types of combustors (e.g., those maintaining a rich or stoichiometric fuel/air ratio in the primary combustion zone) the combustor liner temperatures increase significantly with decreasing fuel hydrogen content. Newer combustor designs incorporating airblast fuel nozzles and leaner primary combustor zones have been found to be significantly less sensitive to the hydrogen content of the fuel. The newer combustor designs evaluated have primarily been on high pressure ratio engines. The decreased sensitivity of the combustor liner temperature to the hydrogen content of the fuel may be caused by: (1) The formation of less soot due to the improved fuel evaporation and mixing obtained with the higher temperature compressor discharge air and the use of the airblast nozzles, and (2) the combustion flame emissivity in high pressure ratio engines is already close to unity, and increasing the amount of soot formed causes only a small increase in the flame emissivity.

FREEZING POINT RELATIONSHIPS OF JET FUELS

by: Wilbur Affens

Naval Research Laboratory

INTRODUCTION

Jet aircraft are frequently exposed to low operating temperatures, and it is therefore essential that their fuels do not freeze and plug filters at these temperatures. For this reason, jet fuel specifications include freezing-point-maximum requirements, as are shown in Slide 1. This can create a problem for the Navy, since it is not always practical to produce JP-5 from available crudes which can meet both the freezing point and flash point requirements. This problem can occur both with conventional JP-5 (from petroleum) or with JP-5 from syncrudes.

The low temperature properties of jet fuels (freezing point, pour point and viscosity), as well as many other properties, are controlled by composition. The questions which are being addressed in this work are: what is the nature of the components of jet fuel which result in high freezing points? and, what is the origin of these components in the crudes from which they are processed?

Earlier work by Dimitroff (1) found that the saturate fraction of fuels exerted the greatest influence on freezing point, but that the aromatic fraction was also important. Subsequent work at NRL (2) has shown that the freezing point of a fuel is not a simple function of any particular component, but that all components play a part. Nevertheless, it was shown that the higher *n*-alkanes appear to exert a major influence on the freezing point of fuels. This paper is in two parts. The first deals with the relationship of freezing point to composition of JP-5 jet fuel in order to better understand fuel properties. The second part is concerned with tracing the origins of *n*-alkanes in jet fuel.

FREEZING POINTS OF PURE COMPOUNDS

The freezing point of a pure compound is the temperature at which solid crystals of the substance are in equilibrium with the liquid phase under its own vapor pressure. Depending on whether the equilibrium is reached by cooling the liquid or heating the solid, it is called the "freezing point" or the "melting point", respectively. Since this equilibrium is independent of the process by which it is attained, these terms are used interchangeably.

The melting of a crystalline solid involves the transition of molecules from an ordered, crystalline lattice to a liquid state of more or less complete disorder. This transition results when the thermal vibrations of the atoms overcome the intermolecular bonding forces in the solid

lattice. Since the intensity of thermal vibration, or temperature, required to overcome the bonding forces is a function of the crystal structure and the intermolecular attractions in the solid, freezing point is therefore dependent on chemical composition and structure.

There is an extensive literature on the effect of composition and constitution on the freezing points of organic compounds. The most widely investigated phenomenon is the effect of increasing carbon number or molecular weight on freezing points for homologous series. Freezing points generally increase with carbon number for a given homologous series, and mathematical expressions have been derived which predict freezing point from molecular weights. Three such relationships are shown graphically in Slide 2 for the *n*-alkanes, *n*-1-olefins, and 2-methyl alkanes (3) which illustrate increasing freezing point as carbon number gets larger. A very interesting phenomenon can also be seen in the graph, namely the alternation of freezing points depending on whether the molecule contains an odd or even number of carbon atoms. The alternation is seen for the lower paraffins (up to C-18), and for the other two series also. It is also noted that the *n*-alkanes have the highest freezing points of the three series.

The effect of isomerization on freezing points is shown for the isomeric hexanes in Slide 3. The freezing points vary from 178° K (*n*-hexane) to 119.5° K (2-methyl pentane). As is frequently the case, the *n*-alkane isomer has the highest freezing point, but as will be shown, this is not always true. For example, in the case of two octane isomers (Slide 4), we note that the freezing point of tetramethyl butane is almost 160°C higher than that of *n*-octane. In general, it is observed that of two isomers, the one with the more compact, or more nearly symmetrical, or more nearly spherical structure, is likely to have the higher freezing point. Such compounds can absorb a considerable amount of rotational energy before their thermal vibrations cause a disruption of the crystal lattice during melting. Another generalization is that side chains discourage crystallization, compared to normal compounds, and thus are likely to have lower freezing points. A summary of some of these generalizations is shown in Slide 5.

FREEZING POINTS OF MULTICOMPONENT SOLUTIONS

Freezing points of solutions introduce an additional variable, the intermolecular forces between different types of molecules. Thus, in the case of solutions, the freezing point is a function of solubility of one or more compounds

in each other. When a solid dissolves in a liquid to form an ideal solution, the process may be considered equivalent to the melting of pure solute at the lowered temperature where solution is taking place. The crystals which form during freezing consist of solid matrices within which a proportionate amount of all liquid constituents are trapped.

Based on equilibrium considerations, assuming ideal solutions, and by use of Raoult's law and the Clausius-Clapeyron equation, the "Ideal Solubility Equations" shown in Slide 6, may be derived. In the equation, X_B , ΔH_F , ΔS_F and T_B are the concentration, heat of fusion, entropy of fusion, freezing point of component "B" respectively; T is the freezing point of the solution, and R the gas constant. It can be seen that the freezing point of a solution depends on the components and their concentrations. Components with high freezing points and/or high concentrations result in solutions with high freezing points.

A plot of $\ln X_B$ vs $1/T$ should therefore result in a straight line, since the other parameters are essentially constant. The slope and intercept can be used to estimate ΔH_F , ΔS_F and also T_B . Several such plots are shown in the next few slides. Slide 7 shows freezing point data for several *n*-alkanes in Isopar M (commercial kerosene type solvent consisting chiefly of isoparaffins). In general, the data does fall on straight lines as predicted by the solubility equation. A similar graph showing solvent effects (non-ideality) for *n*-hexadecane in several different solvents is given in Slide 8. It is seen that decalin is a relatively good solvent, whereas the aromatic 2°-butyl benzene, is a poor solvent. This is shown in tabular form in Slide 9, for 1% solutions (by both weight and mole percent). Slide 10 shows a similar plot for *n*-hexadecane in some alternate JP-5 and Jet-A fuels. The Jet-A fuels (NASA Jet Fuels) do not seem to fall on the line as had been expected based on composition considerations. This question is under study. Slide 11 is a direct plot for tertiary systems showing *n*-tridecane concentrations vs temperature for some solutions of *n*-hexadecane in Isopar M. Two alternate JP-5 fuels containing *n*-hexadecane, COED-4 and Paraho shale fuels are also shown. The change in slope and direction with decreasing C-13 concentration for the solution containing 0.5% C-16 is very interesting and needs to be explained. The lower part of the curve where freezing point decreases with C-13 concentration is unexpected.

Current research is directed toward explaining the anomalies which have been observed. Statistical techniques

are being used in order to obtain a maximum amount of information from a minimum number of multi-component solutions.

ORIGINS OF n-ALKANES IN JET FUELS

Because of the importance of the influence of the higher n-alkanes on the freezing point of JP-5, a study is underway to determine the source of n-alkanes in JP-5 synfuel.

In Slide 12, we see some possible routes for the formation of n-alkanes from crude oil when the oil is thermally stressed such as by pyrolysis and/or cracking. It is seen in the slide that the n-alkanes originally present can be enriched by n-alkane formation from other sources. n-Alkanes can be formed by the cracking of branched alkanes or from cyclic hydrocarbons either directly or via 1-alkenes after subsequent hydrogenation.

Experimental plans for this study are shown in Slide 13. The separation is initiated by a physical separation (fractional distillation) which is not shown on the slide. The distillation cut is then separated by chemical separation techniques by eluting on a silica gel column with suitable solvents. The solvents include n-pentane for the alkanes and other saturates; a solution of benzene: n-pentane (1:3) for the aromatics; and methyl alcohol: benzene solution (1:3) for the polar compounds. This will be followed by pyrolysis treatments. The analysis techniques include Gas Chromatography (GC), GC/Mass Spectrometry, and Proton and C^{13} NMR.

The progress which has been made thus far is shown in Slide 14. Distillation at 300°C at atmospheric pressure, and at 40-mm afford two cuts and the residue is the third. The results of the silica gel separation are shown in the third column. Thus far, the GC treatment of the saturates (upper right) has been completed.

Slide 15 shows a GC trace of n-alkanes and n-olefins in the saturate fraction of a distillate from shale oil. The peaks to the left show the GC response for the solvent and standard respectively (left to right). The bar graph in Slide 16 shows the n-olefin and n-alkane content of the saturate fraction.

From the data obtained thus far, it appears that the n-alkanes and n-1-alkenes in the atmospheric distillate are insufficient to explain the amount of n-alkanes in the fuel. Thus, it seems that a portion of these compounds must be

formed from larger molecules in the processing of the crude oil to obtain jet fuel. This research is continuing.

REFERENCES

1. E. Dimitroff, J. T. Gray, Jr., H. T. Teckel and R. D. Quillian, Jr., "Crystal-Liquid Fuel Phase Intersolubility and Pumpability", Seventh World Petroleum Congress, Mexico City, 2-9 April 1967, Individual Paper No. 47.
2. R. N. Hazlett, J. M. Hall and J. Solash, "Properties and Composition of Jet Fuels Derived from Alternate Energy Sources. Part I. Background and n-Alkane Content," American Chemical Society, Division of Fuel Chemistry., 21 (6), 219-230, San Francisco, CA, 29 August-3 September, 1976.
3. M. R. Cines, "Solid-Liquid Equilibria of Hydrocarbons," Chapter 8, Physical Chemistry of Hydrocarbons, A. Farkas Editor, Vol. I, Academic Press, New York, 1950.

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FREEZING POINTS OF ISOMERIC HEXANES (C₆H₁₄)

HEXANE ISOMER	STRUCTURE	FREEZING POINT (°K)
N-HEXANE	CH ₃ - CH ₂ - CH ₂ - CH ₂ - CH ₂ - CH ₃	177.81
2,2-DIMETHYL BUTANE	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} $	173.28
3-METHYL PENTANE	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \end{array} $	155.15
2,3-DIMETHYL BUTANE	$ \begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \\ \quad \\ \text{CH}_3 \text{ CH}_3 \end{array} $	144.51
2-METHYL PENTANE	$ \begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \\ \text{CH}_3 \end{array} $	119.48

FREEZING POINTS OF TWO ISOMERIC OCTANES (C₈H₁₈)

<u>OCTANE ISOMER</u>	<u>STRUCTURE</u>	<u>FREEZING POINT (°K)</u>
N-OCTANE	CH ₃ - CH ₂ - CH ₂ - CH ₂ - CH ₂ - CH ₂ - CH ₂ - CH ₃	216.36
ISOTETRAMETHYL BUTANE	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} $	373.84

FREEZING POINT VS HYDROCARBON CHEMICAL STRUCTURE

ISOMER WITH HIGHER FREEZING POINT



ALICYCLICS

AROMATICS (PHENYL)

COMPACT HIGHLY SPHERICAL BRANCHED ALKANES
N-ALKANES

SYMMETRICAL BRANCHED ALKANES

ISOMER WITH LOWER FREEZING POINT

ISO-ALKANES (SHORT SIDE CHAINS)

FACTORS WHICH TEND TOWARD HIGHER FREEZING POINTS:

(1) LOW ENTROPY OF FUSION

(2) SYMMETRY

(3) COMPACTNESS

(4) STRAIGHT CHAINS

(5) HIGHLY SPHERICAL STRUCTURE

(6) RIGID MOLECULES

(7) TRANS ISOMERS

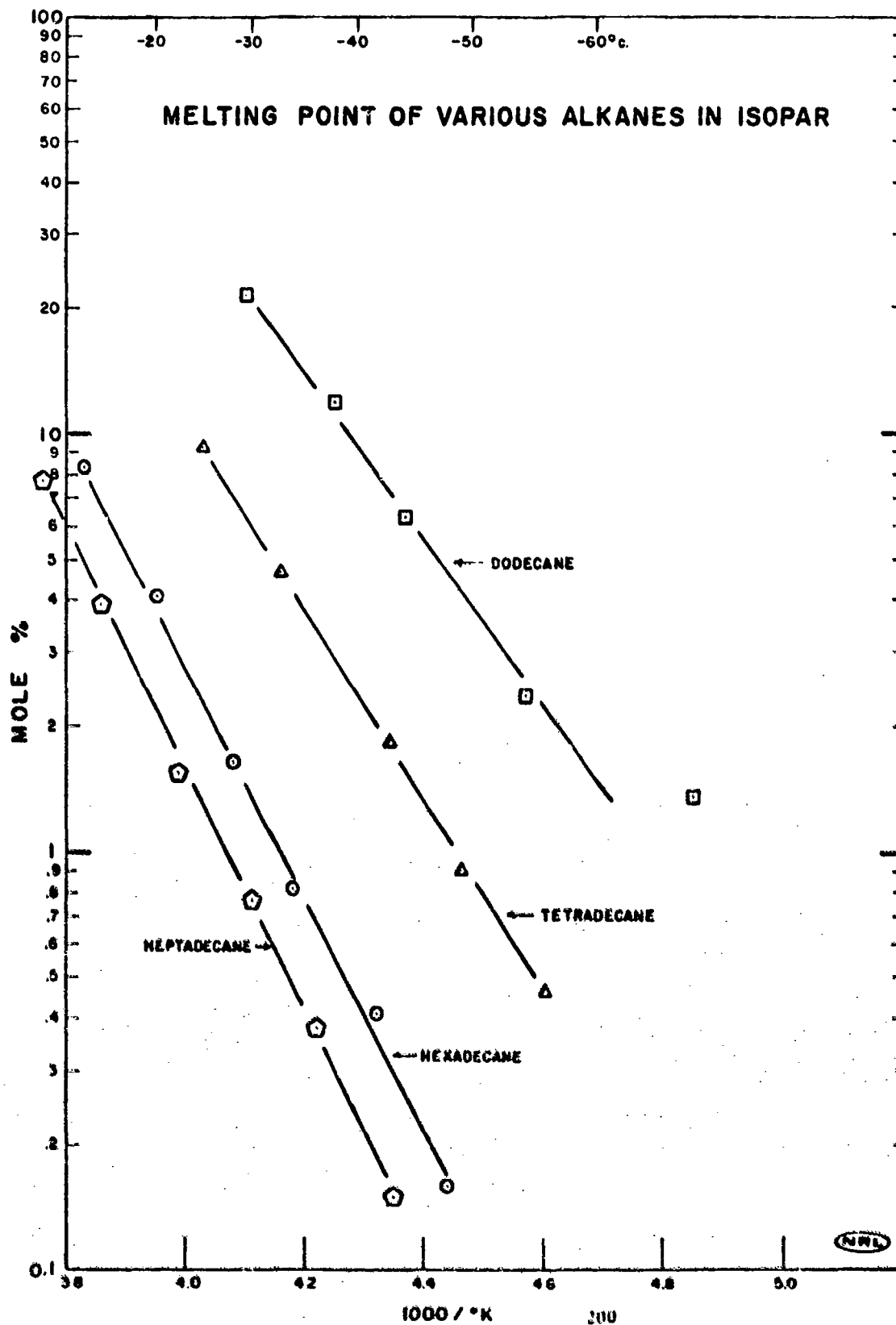
(8) ABILITY TO ABSORB A CONSIDERABLE AMOUNT OF ROTATIONAL ENERGY BEFORE

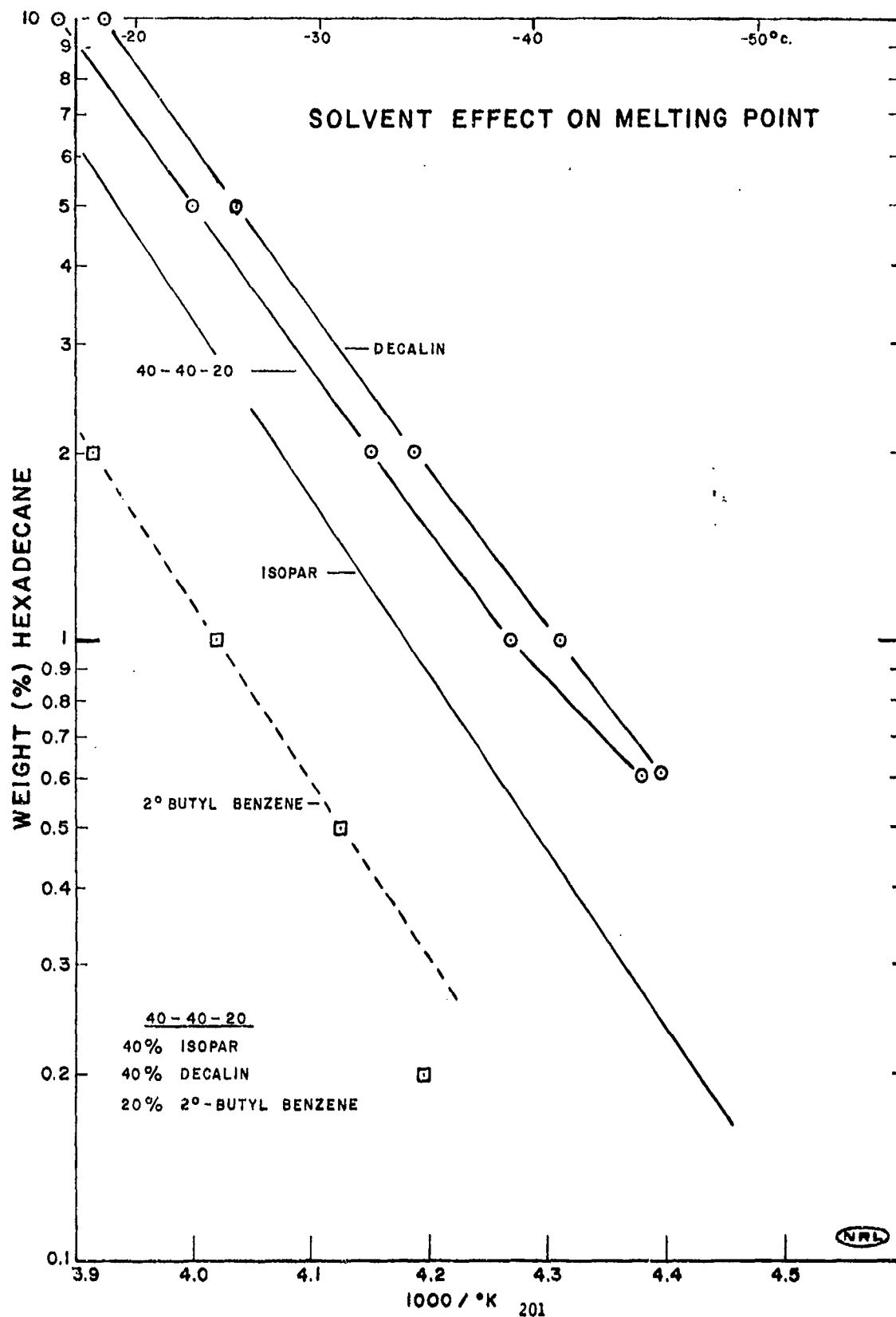
THERMAL VIBRATIONS DISRUPT CRYSTAL LATTICE DURING MELTING

IDEAL SOLUBILITY EQUATIONS

$$\ln x_B = - (\Delta H_F/R)(1/T) + (\Delta H_F/R)(1/T_B)$$

$$\Delta H_F = T_B(\Delta S_F)$$



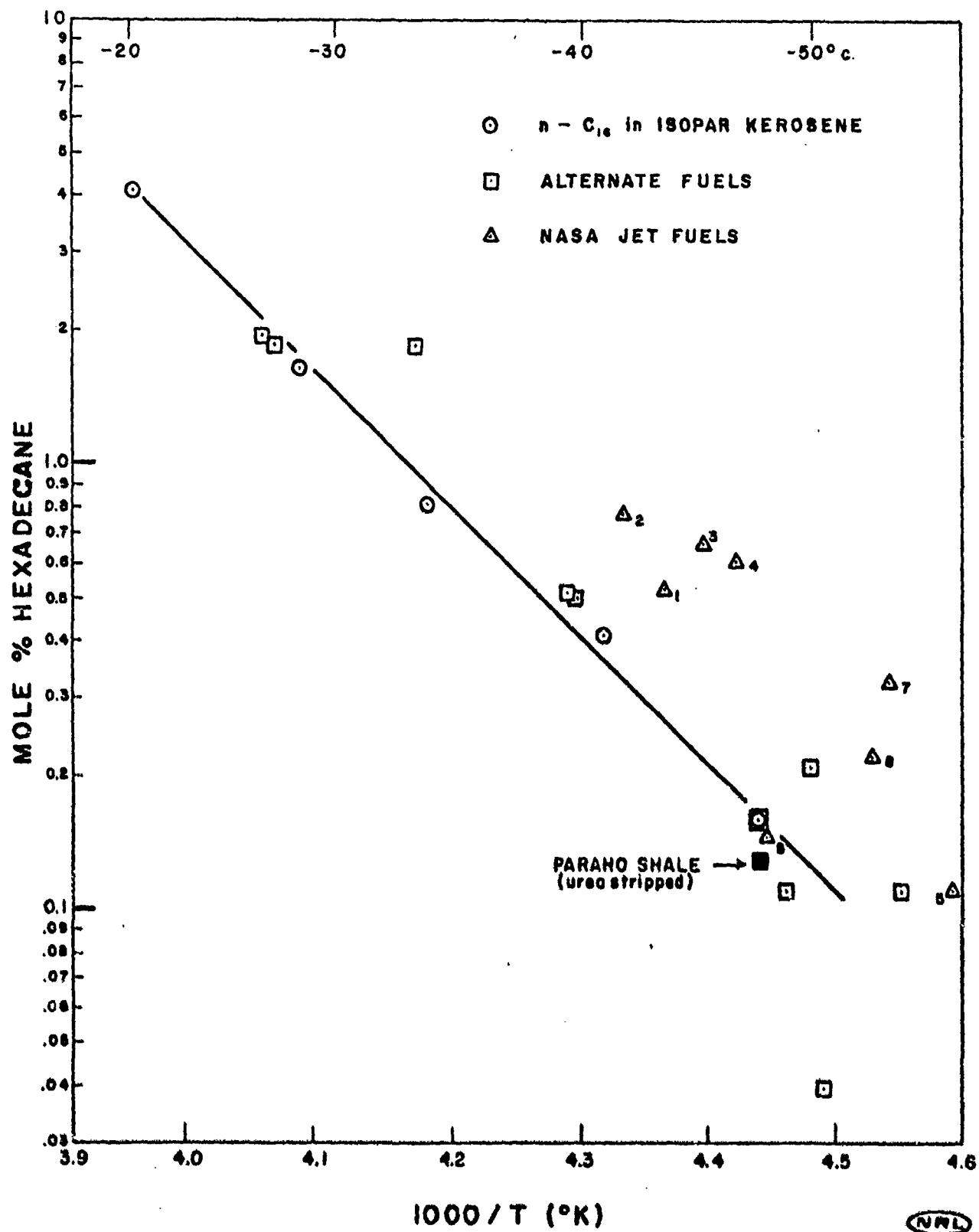


SOLVENT EFFECT ON FREEZING POINT

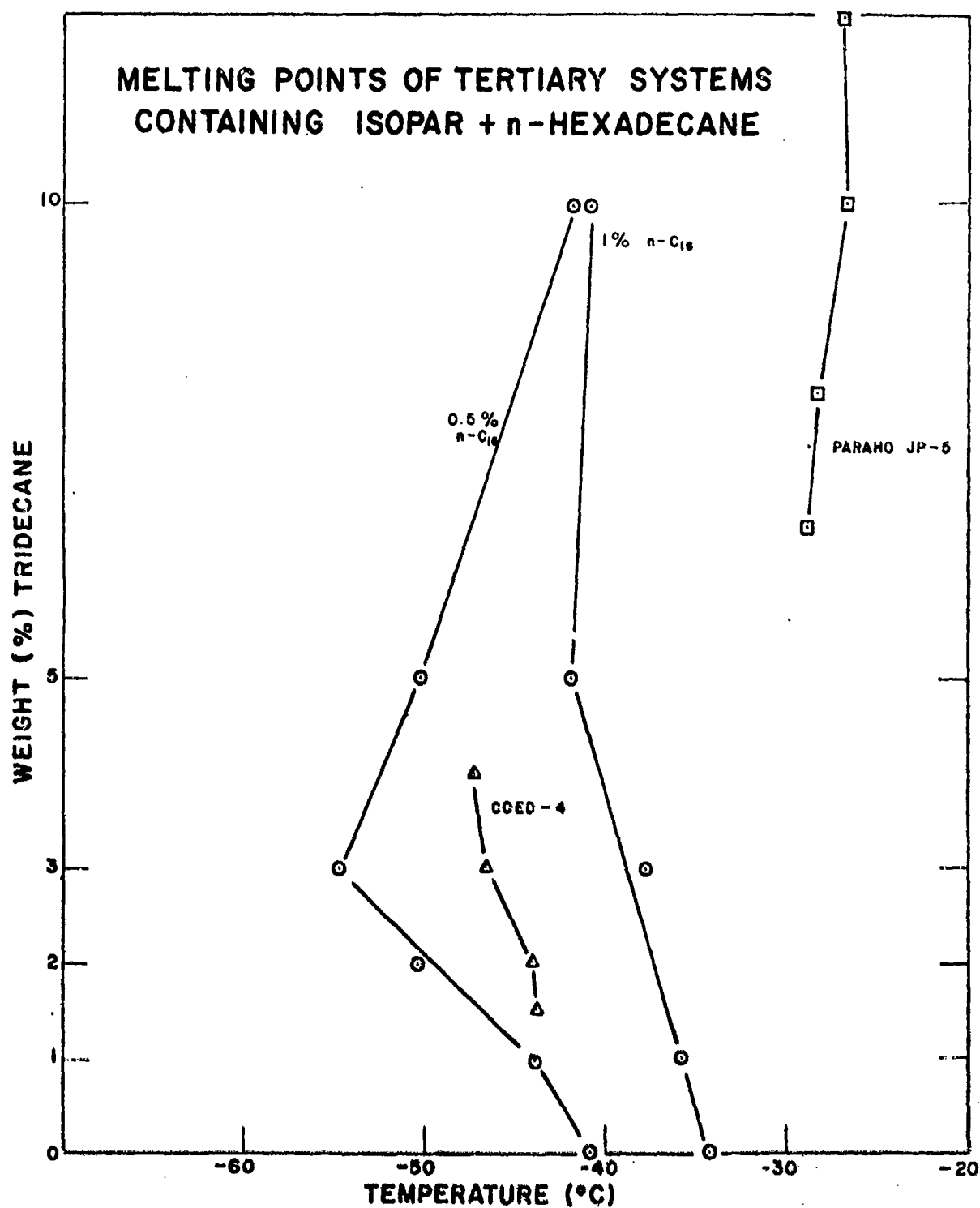
SOLVENT	FREEZING POINT (°C)	
	1.0 WT. % n - C ₁₆	1.0 MOLE % n - C ₁₆
SEC-BUTYLBENZENE	-24	-20
TETRALIN	-29	-25
MIXED-BUTYLBENZENES	-30	-26
20% BUTYLBENZENES IN ISOPAR	-33	-30
ISOPAR	-34	-32
20% TETRALIN IN ISOPAR	-36	-34
40% ISOPAR, 40% DECALIN, 20% TETRALIN	-38	-34
40% ISOPAR, 40% DECALIN, 20% SEC-BUTYLBENZENE	-39	-35
DECALIN	-41	-37
N-HEPTANE	-42	-35

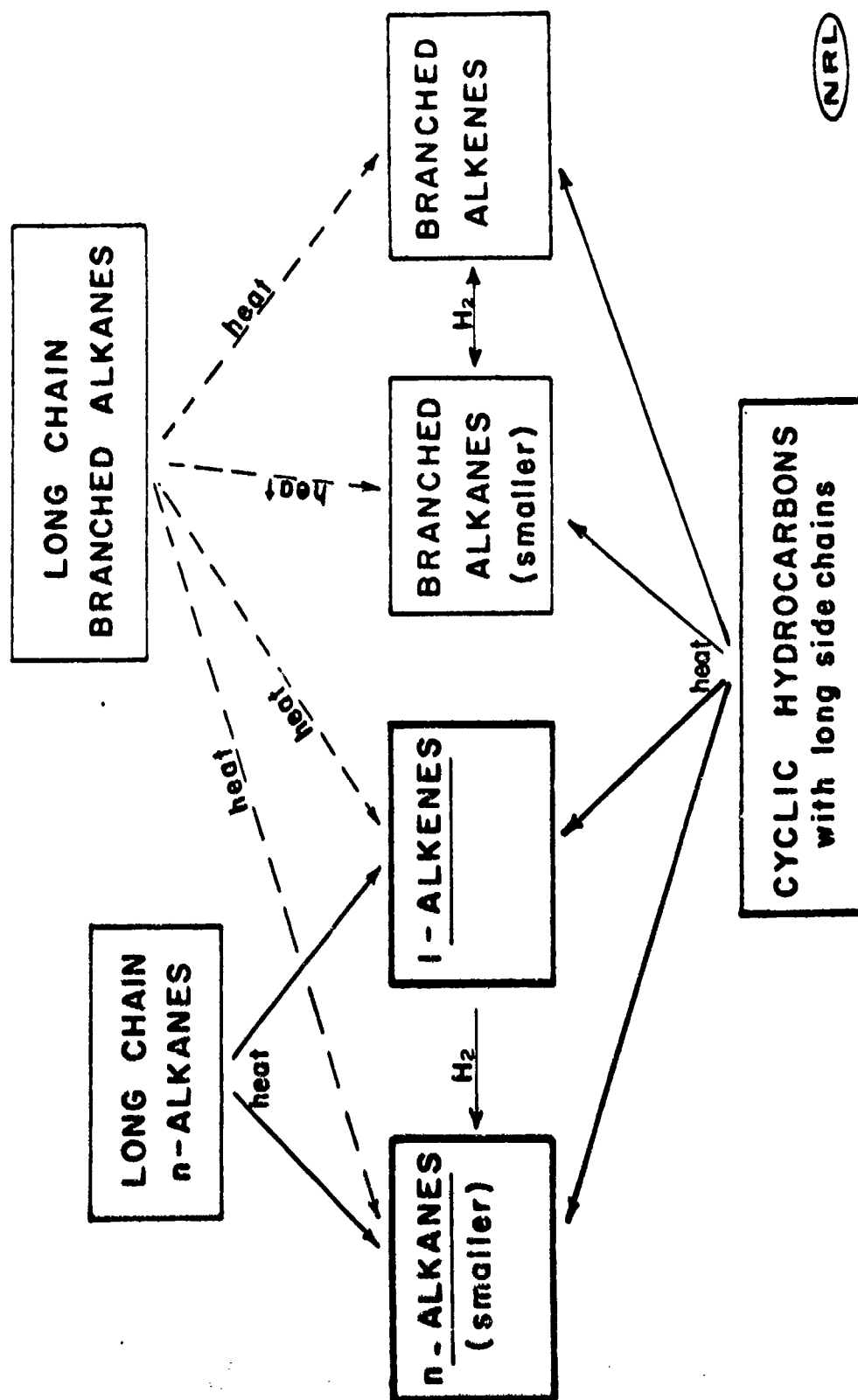
(NRL)

FREEZING POINT OF ALTERNATE JET FUELS



MELTING POINTS OF TERTIARY SYSTEMS CONTAINING ISOPAR + n-HEXADECANE





NRL

EXPERIMENTAL PLANS ORIGINS OF n-ALKANES IN JET FUELS

n-ALKANES
OTHER SATURATES
MONOAROMATICS
DIAROMATICS
POLARS

FRACTIONATION
OF CRUDE BY
FUNCTIONAL GROUP

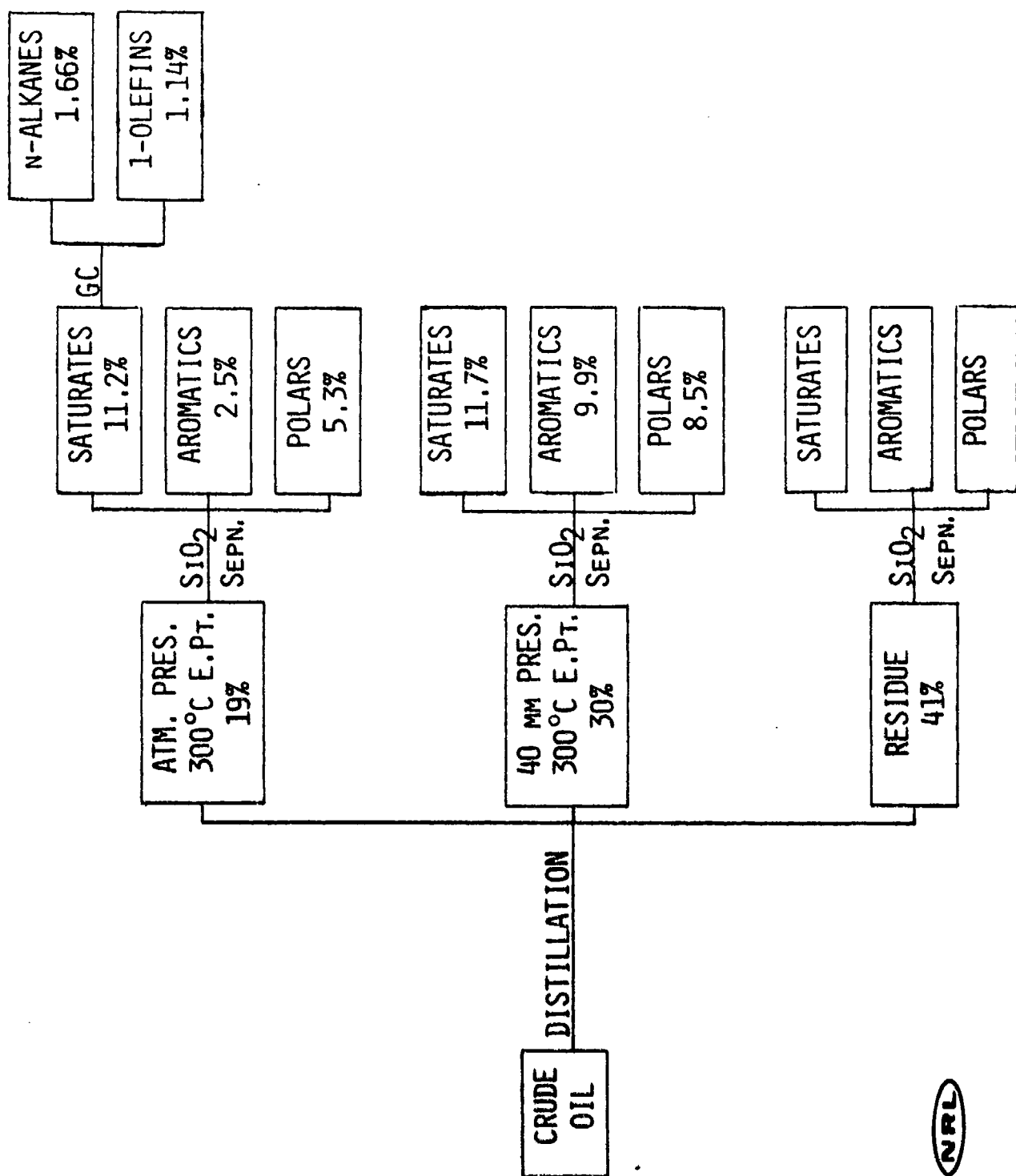
PRODUCT ANALYSIS
FOR
n-ALKANES AND
1-OLEFINS

PYROLYSIS
OF
FRACTIONS AND
MODEL COMPOUNDS

GAS CHROMATOGRAPHY
COMBINED GC/MS
PROTON & C¹³ NMR

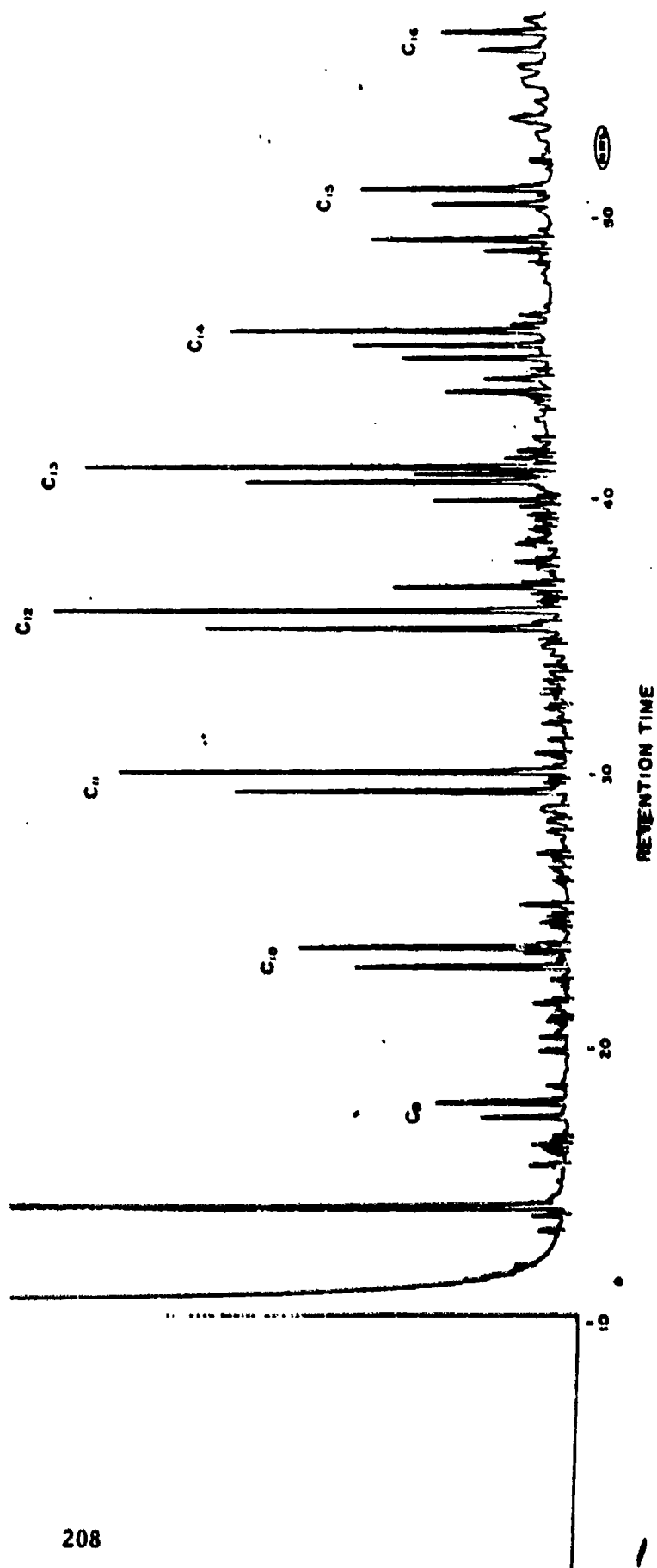
ANALYSIS
TECHNIQUES

FRACTIONATION AND SEPARATION OF PARAHO SHALE OIL



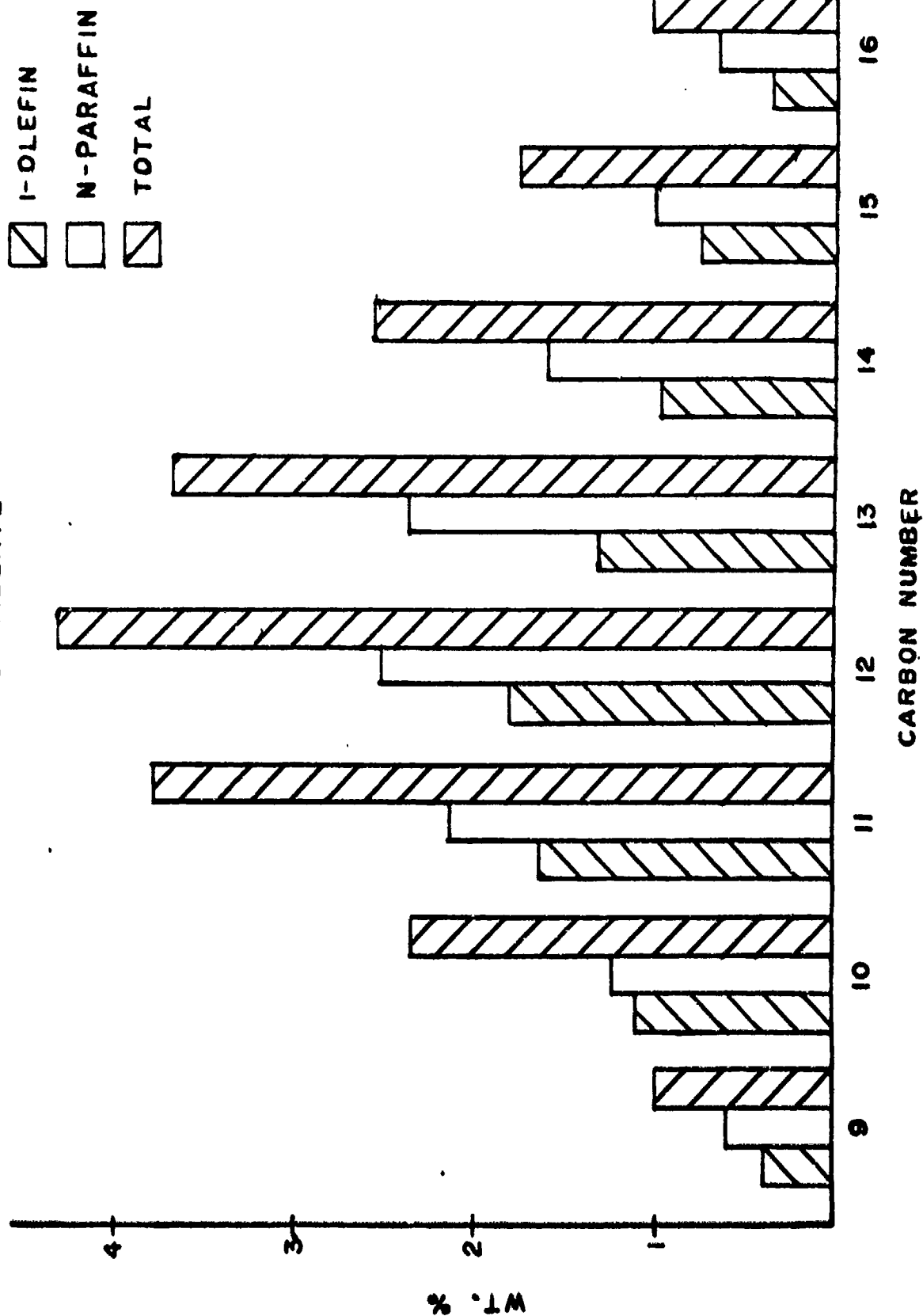
**GAS CHROMATOGRAM SHOWING N-ALKANES
AND I-OLEFINS IN SATURATE FRACTION
OF DISTILLATE CUT FROM SHALE OIL**

END POINT - 300°C



N-ALKANE AND I-OLEFIN CONTENT OF SHALE OIL SATURATE FRACTION

--100-300°C DISTILLATE--



COMPOSITION AND TEMPERATURE DEPENDENCE
OF SHEAR VISCOSITY OF HYDROCARBON MIXTURES

by: Cornelius T. Moynihan

Vitreous State Laboratory
Catholic University of America

INTRODUCTION

Characterization of fuel viscosities is important because the viscosity directly controls atomization in combustors and affects the performance of other engine components such as fuel pumps. Jet aircraft fuels are complicated mixtures of saturated, unsaturated and aromatic hydrocarbons and may be exposed to temperatures ranging from -55 to 50°C. Consequently an understanding of jet fuel viscosities useful from an engineering standpoint demands an account of the combined effects of temperature and composition.

Considerable work has been done in the past on the temperature dependence of organic liquid shear viscosities and some work on the composition dependence. However, very little has been done on the combined temperature-composition dependence over temperature ranges where the shear viscosity may change by an order of magnitude or more, as it can over the operating temperature range of jet fuels. In the next section, we will describe some recent NAVAIR sponsored research⁽¹⁻³⁾ on the temperature-composition dependence of shear viscosities of hydrocarbons used for high energy density missile fuels.

FREE VOLUME TREATMENT OF VISCOSITIES OF HYDROCARBON MISSILE FUELS

The structures of the missile fuel hydrocarbons whose viscosities were studied are shown in Fig. 1. Arrhenius plots of the temperature dependence of the shear viscosity η are shown for two of the compounds in Fig. 2; as is typical of organic liquids in this viscosity range, the plots are non-linear and concave upwards. The temperature dependence of η can be well

described by the Vogel-Tammann-Fulcher (VTF) equation:

$$\ln \eta = A + B/(T-T_2) \quad (1)$$

where A, B and T_2 are constants.

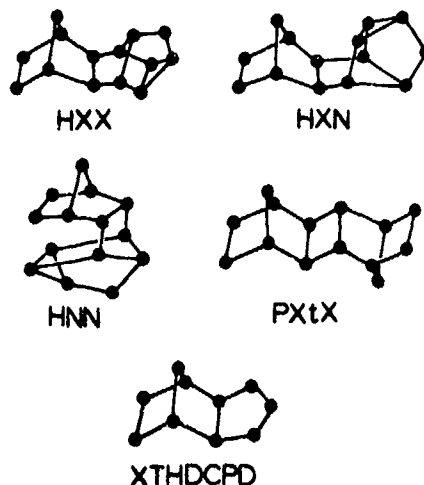


Figure 1. Structures of compounds studied in the present paper: hexacyclic *exo,exo*-dihydrodinorbornadiene (HXX), hexacyclic *endo,endo*-dihydrodinorbornadiene (HNN), hexacyclic *exo,endo*-dihydrodinorbornadiene (HXN), pentacyclic *exo-trans-exo*-tetrahydrodinorbornadiene (PXtX), *exo*-tetrahydrocyclopentadiene (XTHDCPD).

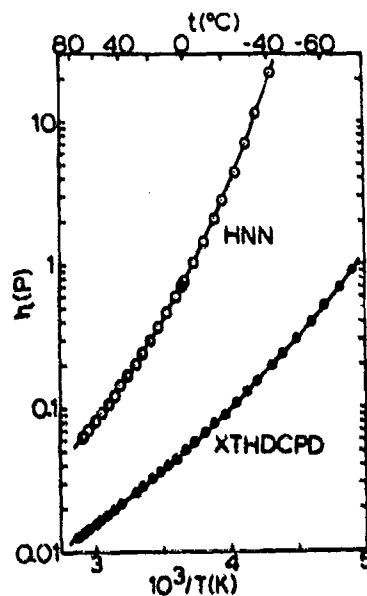


Figure 2. Arrhenius plots of shear viscosities of HNN and XTHDCPD. Solid lines are calculated using least-squares VTF equation parameters.

In Fig. 3 are shown viscosity isotherms for the HNN-XTHDCPD system at several temperatures. Note the logarithmic viscosity scale and the curvature of the isotherms. This means that simple relations such as $\sum X_i \eta_i$ (additive viscosities), $1/\sum X_i/\eta_i$ (additive

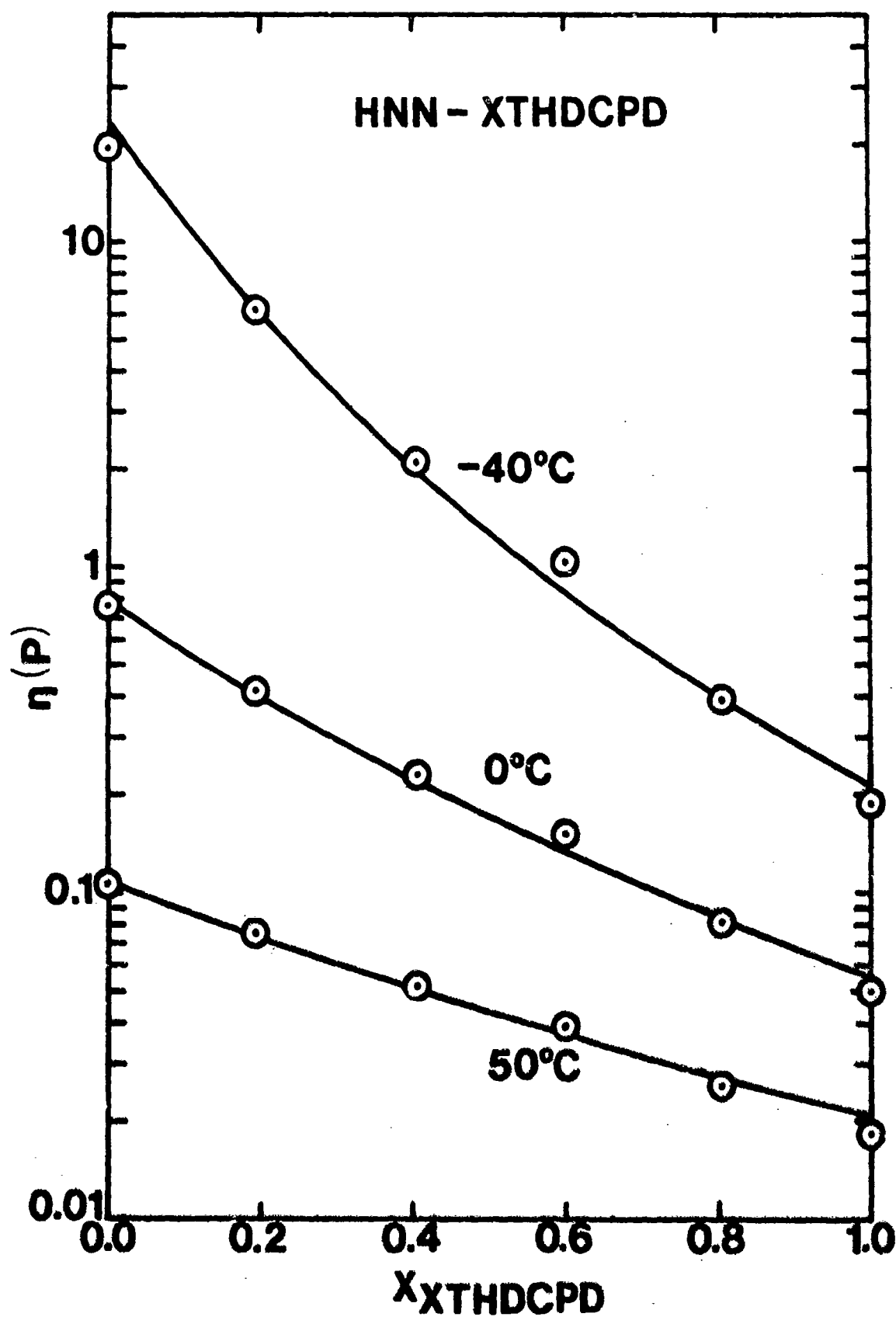


Fig. 3 Shear viscosity isotherms for the HNN-XTHDCPD system. Solid lines are calculated from Eq. (8).

fluidities, or $\exp(\sum X_i \ln \eta_i)$ (additive logarithms of viscosities or fluidities) cannot account for the composition dependence of the viscosity, where X_i is the mole fraction of component i .

Of the simple theories the free volume treatment^(4,5) has been most successful in accounting for the temperature dependence of organic liquid viscosities in the 10^{-2} to 10^4 P range. According to this theory, the shear viscosity is given by

$$\ln \eta = \ln [(mkT/8\pi)^{1/2}/\beta a_0^2] + \gamma v^*/v_f \quad (2)$$

where a_0 is the molecular diameter, β is the fraction of a_0 travelled by a molecule in a diffusive step, m the molecular mass, k the Boltzmann constant, v^* the critical local free volume that must be available for a diffusive step to occur, and γ a factor of the order unity which accounts for overlap of free volume between neighboring molecules. The free volume v_f of the liquid is given by

$$v_f = v\Delta\alpha(T-T_2) \quad (3)$$

where v is specific volume, $\Delta\alpha$ the difference between liquid and glass thermal expansion coefficients, and T_2 a temperature at which the free volume at equilibrium is zero. If we combine Eqs. (2) and (3) and ignore the weak temperature dependence due to the $T^{1/2}$ in the first term on the right hand side of Eq. (2), we obtain an expression of the form of the VTF equation, Eq.(1).

Granted that molecular diameters, a_0 , of low molecular weight organic molecules are all of comparable magnitude, Eq. (2) shows that the most critical factor in determining the shear viscosity of a liquid at a given temperature is the free

volume, v_f . When two or more liquids are mixed to form a solution, the resulting free volume per molecule will in general be different from that of the various pure components. As a consequence, the contribution of a given component to the viscosity of the solution will be determined by the net free volume of the solution and not by the free volume of the pure component. This suggests a straight forward modification to Eq. (2) to give mixture viscosities as a function of temperature and composition:

$$\ln \eta = \sum X_i \{ \ln[(mkT/8\pi)^{1/2}/\beta a_{oi}^2] + \gamma v_i/v_f \} \quad (4)$$

where v_f , the net free volume of the mixture, is assumed to be additive in terms of the component free volumes:

$$\begin{aligned} v_f &= \sum X_i v_{fi} = \sum X_i v_i \Delta \alpha_i (T - T_{2i}) \\ &\approx v \Delta \alpha (T - \sum X_i T_{2i}) \end{aligned} \quad (5)$$

The approximation in Eq. (5) results from the fact that $v \Delta \alpha$ has very similar values for most organic liquids. Combining Eqs. (4) and (5) and again ignoring the weak $T^{1/2}$ temperature dependence in the first set of terms on the right side of Eq. (4), we get a general VTF equation for the temperature-composition dependence of viscosity of the form:

$$\ln \eta = \sum X_i [A_i + B_i / (T - \sum X_i T_{2i})] \quad (6)$$

Note that Eq. (6) contains no more adjustable parameters than are required to describe the temperature dependence alone of the pure components of the mixture.

Eq. (6) was tested on mixtures of the four NBD hydrogenated dimers shown in Fig. 1. Since these compounds are so similar, it was found that Eq. (6) could be applied in a simpler form:

$$\ln \eta = \sum X_i A_i + B/(T-T_2) \quad (7)$$

That is, the same value of B_i and T_{2i} could be used for each component. The parameters A_i , B and T_2 were determined by computer fit to mixture viscosities. According to Eq. (7) a plot of $\log (\eta / \exp \sum A_i X_i)$ vs. $1/(T-T_2)$ should put viscosity data for all compositions on the same linear plot, as is shown to be the case in Fig. 4. Molecular diameters a_{oi} (Table I) from the A_i parameters via Eq. (6) were in good agreement with the maximum molecular dimensions determined from scale models. Note that for this set of similar, rigid molecules, the smaller the molecule, the larger the viscosity at a given temperature. A more detailed description of this study is given in Ref. 2.

Table I. Comparison of molecular diameters calculated from viscosity and maximum molecular dimensions from scale models for NBD hydrogenated dimers.

<u>Compound</u>	a_o (nm)	maximum
	<u>from viscosity</u>	<u>molecular dimension (nm)</u>
HXX	0.92	1.06
HXN	0.80	0.95
HNN	0.77	0.88
PXTX	0.91	1.05

Eq. (6) was also tested by applying it to mixtures of the NBD hydrogenated dimers with the lower molecular weight XTHDCPD. Here Eq. (6) could be simplified to the form

$$\ln \eta = \sum A_i + B/(T - \sum X_i T_{2i}) \quad (8)$$

The same value of T_{2i} (=153K) could be used for each of the four

NBD hydrogenated dimers, while the XTHDCPD had a lower T_{21} ($= 95K$). The same value of B could be used for all five components.

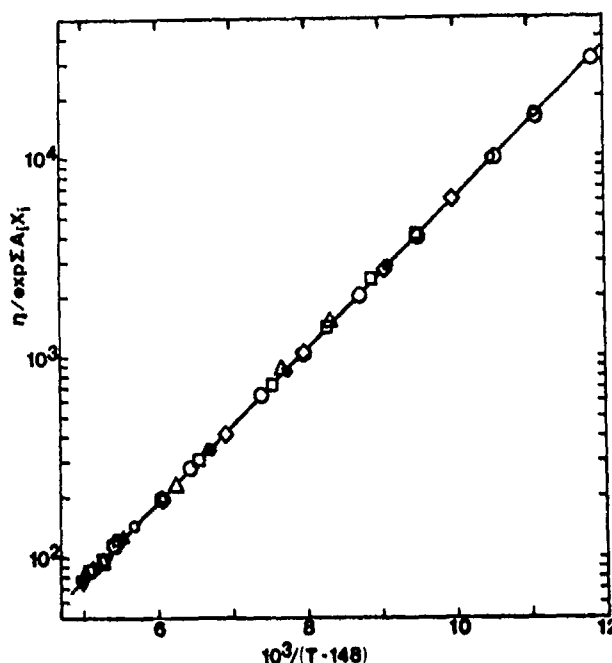


Figure 4 Master viscosity-composition-temperature plot for NBD hydrogenated dimers and their mixtures.

The solid lines in Fig. 3 are calculated from the parameters for the best fit of the viscosity data to Eq. (8).

PROPOSED RESEARCH ON VISCOSITIES OF JET FUEL COMPONENTS

In the coming year under a NAVAIR sponsored research contract we intend to investigate the composition and temperature dependence of mixtures of molecules typical of those found in jet fuels. The purpose is to discover the degree to which semi-empirical equations such as Eq.(6) can be used to account for the viscosities and possibly to clarify the contributions of the sizes, shapes and molecular structures to mixture viscosities. In Table II are listed a number of C_{10}

hydrocarbons typical of the molecules to be investigated, along with the pure liquid densities and viscosities taken from the literature. Some trends in viscosity are apparent already from this data. First, the higher the viscosity at a given temperature, the higher the temperature dependence on a logarithmic scale (compare Fig. 2). Second, the longer the maximum dimension of the molecule, the lower the viscosity, as was found to be the case with the NBD hydrogenated dimers (See Table I). On the other hand, some of the molecules in Table II possess flexibility lacking in the rigid molecules of Fig. 1, and it also appears that the more configurations a molecule can assume, the lower the viscosity. Which, if either, of these two factors is predominant in determining the viscosity and how these factors act in contributing to mixture viscosities will hopefully be elucidated by our studies in the coming year.

Acknowledgement








The research reported here was sponsored by contracts from the Naval Air Systems Command.

References

1. C. T. Moynihan, H. Sasabe, D. Czaplak and U. E. Schnaus, Chem. Eng. Data, 23, 107 (1978).
2. C. T. Moynihan, U. E. Schnaus and D. Czaplak, J. Phys. Chem., 82, 1087 (1978).
3. C. T. Moynihan, U. E. Schnaus, H. Sasabe and D. Czaplak, Final Technical Rep., NAVAIR Contract No. N00019-77-C-0065, Dec., 1977.
4. M. H. Cohen and D. Turnbull, J. Chem. Phys., 31, 1164 (1959).
5. M. Cukierman, J. W. Lane and D. R. Uhlmann, J. Chem. Phys., 59, 3639 (1973).

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Table II. Shear viscosities and densities of C₁₀ hydrocarbons

hydrocarbons	ρ (g/cm ³) @ 25°C	η (cP)		
		25°C	0°C	-25°C
1-decene 	0.737	0.76	1.13	----
n-decane 	0.726	0.86	1.30	2.45
n-butyl benzene 	0.856	0.96	1.48	2.65
n-butyl cyclohexane 	0.796	1.21	1.90	3.57
trans-decalin 	0.866	1.94	3.23	----
exo-tetrahydro dicyclopentadiene 	0.925	2.72	4.70	9.67
cis-decalin 	0.893	3.03	5.62	----

BEHAVIOR AND INTERACTIONS
OF
JET FUEL ADDITIVES

C. P. HENRY (DuPont Co.)

GENERAL

FLOW IMPROVERS

CORROSION INHIBITORS/
LUBRICITY ADDITIVES

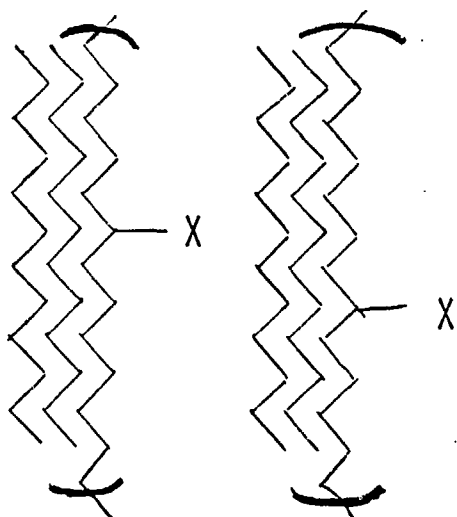
STORAGE STABILIZERS

THERMAL STABILITY
ADDITIVES

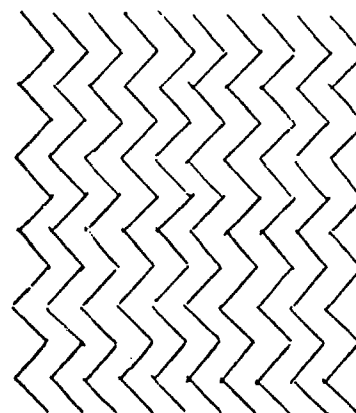
CONDUCTIVITY
IMPROVERS

- ADDITIVE PERFORMANCE DEPENDS ON SPECIFIC FUEL CHARACTERISTICS
- TESTING IN SEVERAL FUELS IS ADVISABLE
- FOR "APPROVAL", INTERACTIONS MUST BE MINIMAL OR PREDICTABLE - BUT MAY NOT HAVE BEEN EXPLORED AS A FUNCTION OF FUEL CHARACTERISTICS FOR ALL POSSIBLE COMBINATIONS OR SPECIFICATION TESTS.
- SPECIAL TEST RESULTS SHOULD BE LIMITED TO SPECIFIC USE REQUIREMENTS.

MECHANISM



WITH FLOW IMPROVER:
MICROCRYSTALS



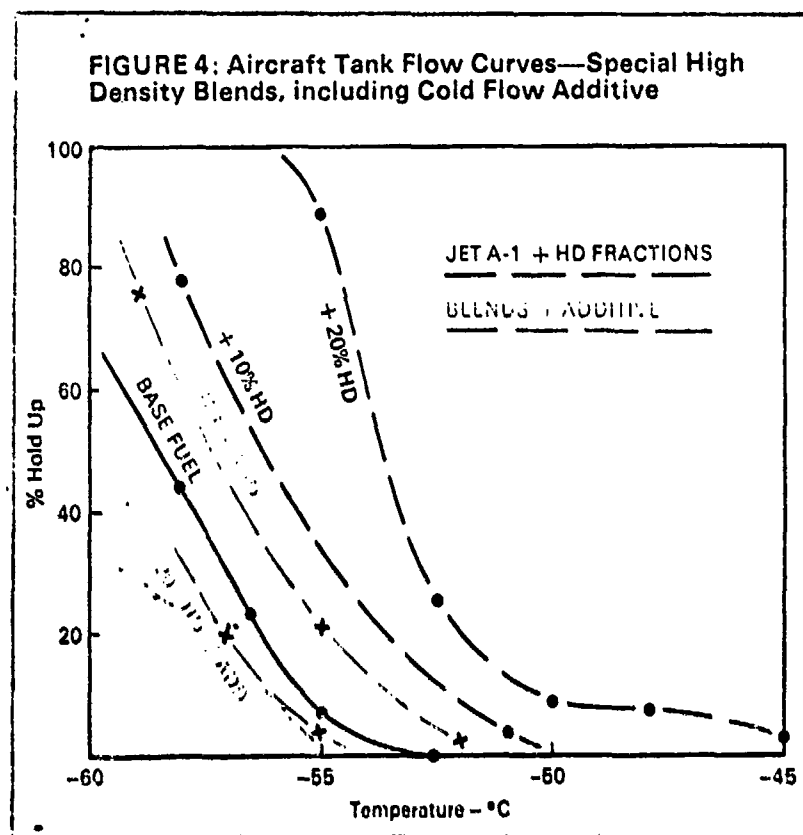
NO FLOW IMPROVER:
LARGE INTERLOCKING PLATES

- POLYMERS ARE EFFECTIVE WHERE $X = \text{CH}_3, \text{OAc}, \text{Cl}$
- EFFECTIVE POLYMER CHARACTER DEPENDS ON WAX TYPE
 - HEAVY HYDROCARBONS - C_{10} TO C_{42} WAX
 - 100-1000 PPM OF A 1200 CARBON POLYMER
 - MIDDLE DISTILLATES - C_{12} TO C_{26} WAX
 - 25-200 PPM OF A 120 CARBON POLYMER

FLOW IMPROVERS (CONT'D)

JET FUELS

- HIGH END POINT JET FUELS
 - CONTAIN MIDDLE DISTILLATE TYPE WAXES
 - MIDDLE DISTILLATE FLOW IMPROVERS EFFECTIVE



FROM P. T. FORD AND A. G. ROBERTSON, SHELL AVIATION NEWS
441, 1977

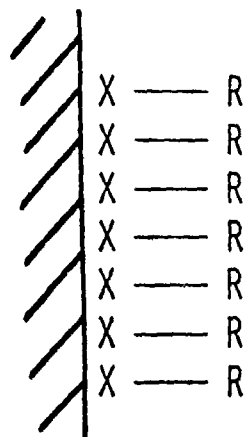
JET FUEL FLOW IMPROVERS (CONT'D)

- NORMAL END POINT JET FUELS, WITH ABNORMAL CONC. OF
C₁₀-C₁₆ WAX
 - TYPE OF EFFECTIVE FLOW IMPROVER UNDEFINED

- SIDE PROPERTIES AND ADDITIVE INTERACTIONS ARE
UNDEFINED

CORROSION INHIBITOR/LUBRICITY ADDITIVES

MECHANISM



X = COOH, COMPLEX PHOSPHATE

DICARBOXYLIC ACIDS MOST COMMON TYPE

- HIGHLY POLAR GROUPS STRONGLY SURFACE-ADSORBED
- PROVIDES A TENACIOUS FILM WHICH PREVENTS ELECTROLYTE ACCESS TO SURFACE
- FILM LESS READILY DISPLACED THAN OIL (MILD BOUNDARY LUBRICANT)

EFFECTIVENESS

- 3-24 PPM PROVIDES GOOD CORROSION INHIBITION
- 8-24 PPM PROVIDES GOOD LUBRICITY

SIDE PROPERTIES

- 13 USAF QPL ADDITIVES, PROPERTIES VARY AND CAN BE FUEL-DEPENDENT
- MILD SURFACTANTS, SOME WSIM LOSS
- PHOSPHORUS-CONTAINING TYPES AFFECT THERMAL STABILITY AT EXTRAORDINARILY HIGH TEST TEMPERATURES
- SOME FUEL FILTERABILITY LOSS WITH SALT WATER CONTACT
- EXCESSIVE CONCENTRATIONS CAN LOOSEN METAL SCALE

ADDITIVE INTERACTIONS

- VARIABLE WSIM LOSS WITH SOME ANTIOXIDANTS
- VARIABLE CONDUCTIVITY AND WSIM LOSS WITH CONDUCTIVITY IMPROVERS.
- INTERACTIONS WITH RESPECT TO CHARACTERISTICS OTHER THAN CONDUCTIVITY, WSIM NOT WELL EXPLORED.

STORAGE/THERMAL STABILITY ADDITIVES

ANTIOXIDANTS

- ACT AS FREE RADICAL SCAVENGERS: INTERRUPT CHAIN PROPOGATION STEPS OF FREE RADICAL FUEL OXIDATION
- MOST SIGNIFICANT BENEFITS OCCUR WHEN NATURAL RADICAL SCAVENGERS ARE ABSENT (SEVERELY HYDRO-TREATED FUEL)
- VARIABLE EFFECTIVENESS
- TYPICAL CONCENTRATIONS 18-24 PPM
- HINDERED PHENOL ANTIOXIDANTS
 - LOW CHEMICAL REACTIVITY LIMITS SIDE EFFECTS, INTERACTIONS - INNOCUOUS AT WORST
 - MIGHT BE BENEFICIAL AT CONCENTRATIONS EXCEEDING 24 PPM
 - NOT REMOVED BY CLAY FILTRATION
 - VARIETY AVAILABLE.
- PHENYLENEDIAMINE ANTIOXIDANTS
 - SOMETIMES DELETERIOUS IN HIGH TEMPERATURE TESTS
 - MORE EFFECTIVE FREE RADICAL SCAVENGERS IN SOME FUEL TYPES
 - COLOR FUEL, REMOVED BY CLAY FILTRATION
 - SIDE EFFECTS AND INTERACTIONS MINIMAL, SOMEWHAT GREATER EFFECTS THAN FOR PHENOLICS
 - TWO TYPES: DI-ISOPROPYL, DI-SEC-BUTYL

STORAGE/THERMAL STABILITY ADDITIVES (CONT'D)

METAL DEACTIVATOR

- INHIBITS CATALYSIS OF FUEL OXIDATION BY DISSOLVED COPPER SALTS
- UP TO 6 PPM USED, MORE MAY BE BENEFICIAL
- SOMETIMES IMPROVES STORAGE STABILITY IN THE ABSENCE OF COPPER - MECHANISM UNKNOWN
- MINIMAL KNOWN SIDE EFFECTS, INTERACTIONS
- PRINCIPAL TYPE N,N'-DISALICYLIDENE-1,2-PROPANE DIAMINE

METAL PASSIVATORS

- PASSIVATES COPPER SURFACES
- USE CONCENTRATION UP TO 10 PPM
- SIDE EFFECTS, INTERACTIONS NOT WELL STUDIED
- PRINCIPAL TYPE: BENZOTRIAZOLE

STORAGE/THERMAL STABILITY ADDITIVES (CONT'D)

DISPERSANTS

- COLLOIDALLY SUSPEND DEGRADATION PRODUCTS
- NO DEPENDENCE ON DEGRADATION MECHANISM
- DISPERSANTS CAUSE WATER EMULSION; NOT ACCEPTABLE TODAY
- ADDITIVE INTERACTIONS NOT SUBSTANTIAL FOR NO. 2 FUELS; UNKNOWN FOR JET FUELS

JFA-5 (A.O./DISPERSANT/MD)

- IMPROVES THERMAL STABILITY TEST RESULTS
- 3 TO 4 LB/1000 BBL REQUIRED FOR JPTS FUEL (MIL-F-25524B)
- WATER SEPARATION TRADE-OFF MAY BE ACCEPTABLE AT UP TO 5 LB/1000 BBL (14 PPM)

OTHER ADDITIVES

- CONSIDERABLE LITERATURE AND PATENTS ON OTHER STORAGE OR THERMAL STABILITY ADDITIVES
- GENERAL EFFECTIVENESS NOT WELL DEFINED
- INTERACTIONS, SIDE PROPERTIES NOT WELL DEFINED

CONDUCTIVITY IMPROVERS

- WILL PROBABLY BE REQUIRED FOR JP-4 FUEL
- PROMOTE RAPID DISSIPATION OF ELECTROSTATIC CHARGE
- CONCENTRATIONS UP TO 2 PPM
- SIDE EFFECTS NOT SIGNIFICANT EXCEPT FOR WSIM SUPPRESSION
- INTERACT WITH SOME CORROSION INHIBITORS WITH RESPECT TO WSIM, CONDUCTIVITY IMPROVEMENT
- TWO ADDITIVES SUITABLE FOR JET FUEL (ASA-3, STADIS[®] 450), OTHERS AVAILABLE FOR MIDDLE DISTILLATES

RECOMMENDATIONS

1. CONSIDER LABORATORY SCREENING TESTS ON REPRESENTATIVE FUELS
FOR EFFECTS OF AVAILABLE ADDITIVES ON
 - CORROSION INHIBITION (LUBRICITY)
 - STORAGE STABILITY
 - THERMAL STABILITY
 - CONDUCTIVITY IMPROVEMENT
 - LOW TEMPERATURE FLOW PROPERTIES
2. DEFINE THE NEED FOR AND ACCEPTABILITY OF FLOW IMPROVERS
 - A SUBSTANTIAL RESEARCH EFFORT WOULD BE REQUIRED TO DEFINE A SUITABLE PRODUCT
 - SIDE PROPERTIES, INTERACTIONS UNKNOWN
3. CONSIDER ACCEPTABILITY OF MULTIFUNCTIONAL ADDITIVES
 - USAF CURRENTLY PROHIBITS PRE-MIXING OF "NEAT" ADDITIVES
 - LIMITS INTERACTION POSSIBILITIES
 - MAY BE MORE ECONOMICAL
 - SUPPLIER CAN ASSURE QUALITY OF OVERALL ADDITIVE PACKAGE
 - MAY BE PARTICULARLY SUITABLE FOR FUELS FROM WELL DEFINED SOURCES AND PROCESSES.

SMOKE SUPPRESSANT ADDITIVES

LARRY MAGGITT

(NAVAL AIR PROPULSION CENTER,
TRENTON, N. J.)

The Naval Air Propulsion Center (NAPC) has been investigating the abatement of jet aircraft exhaust smoke intermittently since 1966. The Navy is concerned about exhaust smoke for two reasons. For one thing, it is a sure giveaway for enemy combatants, especially in low level flight, where the smoke trail is an arrow, pointing out the aircraft for a gunner on the ground. Another obvious reason is the pollution aspect, both in flight and in test cells.

Exhaust smoke consists of small soot particles resulting from inefficient combustion. The optical density of the smoke varies significantly among jet engines. It is affected by combustor design and engine operating conditions, and also varies inversely as a function of the hydrogen content of the fuel. The latter aspect is of concern with respect to possible future synthetic fuels, which may be higher in aromatics that are petroleum derived fuels.

The early efforts on smoke abatement were conducted during the Southeast Asia conflict when avoidance of detection by an adversary was important. A combustor program was initiated as a permanent fix for some engines. Meanwhile, the diesel engine smoke suppressant, Ethyl CI-2 (methyl cyclopentadienyl manganese tricarbonyl), was quickly brought into use as an additive to be injected in flight, on demand.

This additive was successful as a smoke suppressant but had drawbacks in its toxicity and the harmful effects of manganese oxides on turbines. When

it was later decided to use an additive for control of test cell smoke, CI-2 was rejected for these reasons, as well as possible harmful exhaust products. On the basis of prior tests, ferrocene (dicyclopentadienyl iron) was substituted. It was almost as effective as CI-2 and much less troublesome. Of course, test cell modifications and combustor retrofit were also considered.

The use of smoke suppressant additives can have several adverse aspects. As mentioned earlier, some may be toxic in handling. All of the effective products have solid combustion products which can foul fuel nozzles and turbine blades. It is possible that the products of combustion can cause the exhaust gases to be more harmful. And the cost and complexity of test cell operation are increased.

In an effort to minimize the problems and to select the best additive, a number of additives were screened using a gas turbine engine. All depended on a metal for their effectiveness; and relative ranking was based on the quantity of metal required and cost. Ferrocene was still found to be the best known candidate.

A full scale implementation test was then conducted using ferrocene during post overhaul tests of various engines. Automated injection procedures were developed and utilized to minimize the amount of additive used. The limiting operational times before adverse effects on the engines occurred were established. Certain engines were documented for a long range test in which they would be reevaluated after significant service use. The effects on the environment were checked by exhaust gas analysis and stack effluent analysis. It was found that engine deposits definitely limit the

allowable use time, but most smoky engines can be fully tested within the limit without adverse effects. One engine model, the TF41, suffered unsatisfactory deterioration within the time period required for adequate performance testing. The handling safety of the ferrocene was considered satisfactory and no adverse changes in exhaust pollutants were discovered.

At this time, we are satisfied that ferrocene is effective and acceptable for the limited use in test cell operation of certain engines. Actual implementation will depend on the results of other programs attempting to solve the same problem. (The use of water emulsions as well as test cell modifications and clean combustor retrofit).

If smoke suppressant additives are ever to be acceptable for full time use in flight, they must be developed to function with no metal or with a quantity or type of metal that has no effect on the engine. To this end, it would be helpful to learn the mechanisms of smoke inhibition and/or consumption in jet engines. The efficiency of these additives with very highly aromatic fuels has not been determined. Possible beneficial effects on flame radiation should be looked into. Finally, a full evaluation of the effects of any additive on the environment through modification of the exhaust gas pollutants should be made.

JET AIRCRAFT EXHAUST SMOKE

- **DETECTION BY ADVERSARY**
- **AIR POLLUTION STANDARDS**
 - **IN FLIGHT**
 - **IN JET ENGINE TEST CELLS**

FACTORS AFFECTING SMOKE

- **COMBUSTOR DESIGN**
- **ENGINE OPERATING CONDITIONS**
- **FUEL PERCENT HYDROGEN**

HISTORY OF SMOKE ABATEMENT

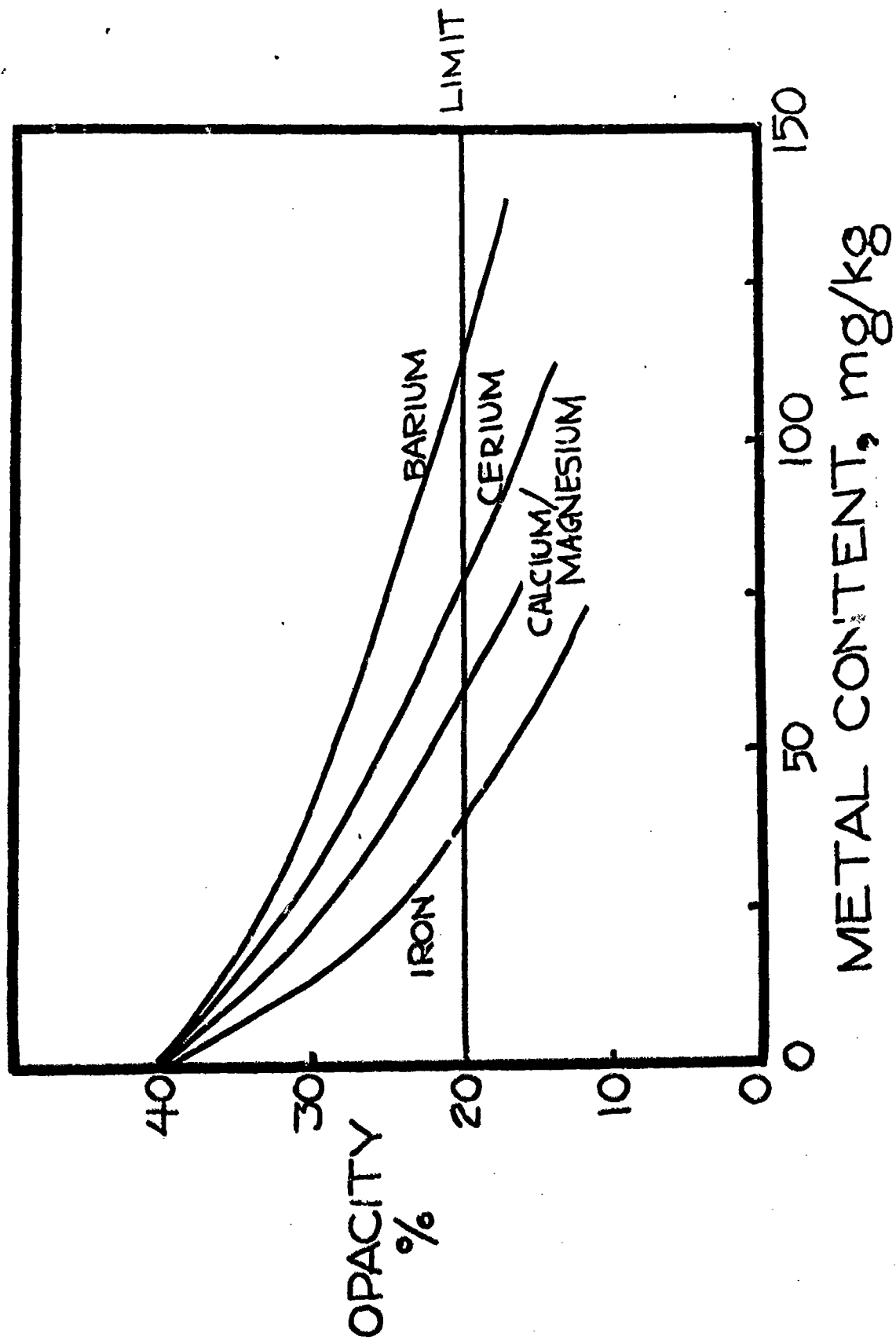
- **INFLIGHT SMOKE ABATEMENT DURING COMBAT**
- **COMBUSTOR REDESIGN/RETROFIT-LONG TERM**
- **FUEL ADDITIVE-SHORT TERM**
 - **CI-2 SELECTED AS MOST EFFECTIVE**
- **TEST CELL SMOKE POLLUTION ABATEMENT**
- **TEST CELL REDESIGN**
- **COMBUSTOR RETROFIT**
- **FUEL ADDITIVE**
 - **FERROCENE SELECTED AS LEAST OBJECTIONABLE**

PROBLEMS IN USE OF SMOKE SUPPRESSANT ADDITIVES

- **SOME CANDIDATES MAY BE TOXIC**
- **COMBUSTION PRODUCTS HARMFUL TO ENGINE**
- **MAY CHANGE NATURE OF EXHAUST GASES**
- **INCREASES COSTS AND COMPLEXITY**

EVALUATION OF NEW SMOKE SUPPRESSANT ADDITIVES

- **EFFICIENCY TESTS**
 - **AMOUNT OF METAL REQUIRED**
 - **COST**
- **IMPLEMENTATION TESTS**
 - **INJECTION PROCEDURES**
 - **EFFECTS ON ENGINES**
 - **EFFECTS ON ENVIRONMENT**
 - **TOXICITY**



EFFECTS OF FERROCENE

- **TURBINE DEPOSITS LIMIT USE**
- **SUITABLE FOR SOME ENGINES DURING TESTS**
- **NOT ACCEPTABLE FOR SOME**
- **TOXICITY OF FUELS WITH FERROCENE NO WORSE THAN
PLAIN FUEL**
- **CONCENTRATIONS AND TYPES OF OTHER EXHAUST POLLU-
TANTS NOT SIGNIFICANTLY CHANGED**

ADDITIONAL WORK REQUIRED

- **DEVELOPMENT OF ADDITIVES FOR FULL TIME USE**
- **INVESTIGATION OF MECHANISMS**
- **DETERMINATION OF:**
 - **EFFECTS ON HIGH AROMATIC FUELS**
 - **EFFECTS ON FLAME RADIATION**
 - **EFFECTS ON ENVIRONMENT**

ANALYSIS OF JET FUELS BY NUCLEAR MAGNETIC RESONANCE

by

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The development of the Fourier transform nuclear magnetic resonance (FT nmr) technique and application to ^{13}C and ^1H nmr during the late 1960's is now a widespread analytical approach for characterizing simple to moderately complex organic compounds. The FT technique has helped alleviate sensitivity limitations which previously was the major limitation in ^{13}C nmr. One of the major advantages of ^{13}C nmr in comparison with the more widely employed ^1H nmr is the greater sensitivity of the ^{13}C chemical shift parameter to subtle changes in molecular structure. For example, the range of ^{13}C chemical shifts for a wide variety of organic compounds is greater than 200 ppm in comparison with ~10 ppm for ^1H nmr. In this presentation, preliminary ^1H and ^{13}C FT nmr data obtained for several fuel samples will be discussed.

Although the Fourier transform nmr technique has largely overcome sensitivity limitation in ^{13}C nmr, until the last 2-3 years quantitative ^{13}C Fourier transform nmr data was not routinely obtained. That is, a number of factors usually alter the simple relationship between signal area and the number of nuclei at resonance in ^{13}C FT nmr. The major factors influencing quantitative ^{13}C measurements in the FT mode are: 1) nuclear Overhauser effects, 2) Spin-lattice relaxation times (T_1 's) and corresponding dependence on pulse repetition rate, 3) Adequate digitization in the frequency domain FT spectrum, and 4) the effects of limited pulse strength (H_1) on the ^{13}C spectral region (ΔF) to be examined.

The nuclear Overhauser effects and variable spin lattice relaxation times (T_1 's) are the factors of primary concern in quantitative ^{13}C FT nmr measurements. To overcome these problems, it has been found that addition

of a paramagnetic relaxation reagent to the nmr sample suppresses the nuclear Overhauser effects and also decreases the T_1 values. This approach of adding a paramagnetic relaxation reagent in conjunction with a ^1H decoupling sequence has been found to provide a convenient method for obtaining quantitative ^{13}C FT nmr data. A similar approach without the ^1H decoupling sequence can be used to obtain quantitative ^1H FT nmr data. If in addition, a weighed standard reference (containing carbon and hydrogen) is added to the sample of interest, this provides a method for obtaining a number of important molecular parameters such as total, aromatic, and aliphatic hydrogen to carbon ratios, $(\text{H/C})_{\text{tot}}$, $(\text{H/C})_{\text{ar}}$ and $(\text{H/C})_{\text{al}}$, respectively. This general approach was adopted to obtain the results for the present study.

To date, six fuel samples listed below derived from petroleum and alternate energy sources have been examined using this approach.

<u>Sample</u>	<u>Source</u>
1) Routine JP-4 (15) obtained from a major refinery	U.S. Air Force
2) A modified JP-4 (01) fuel, a basic petroleum derived JP-4 fuel blended with a highly aromatic solvent (mainly xylenes)	"
3) Routine JP-8 (03)	"
4) Modified JP-8 (05), blended with ~12% of a paraffinic light mineral oil	"
5) COED-5, a coal derived alternate energy fuel	NRL
6) Shale-Paraho, a shale derived energy fuel	"

Generally, these samples exhibit wide differences in molecular properties (e.g., aromaticity ranged from 7-38%). The results obtained

for the two alternate energy jet fuel samples (COED-5 and Shale Paraho) utilizing the quantitative ^1H and ^{13}C FT nmr approach outlined above are summarized in Table I. This data is representative of the type of information obtainable by this approach. An interesting correlation was observed between the freezing point of these fuels (Figure 1) and the average n-alkane size of these fuels as determined by ^{13}C FT nmr.

TABLE I
¹H and ¹³C FT NMR Results for Fuel Samples

Sample	wt. % C	wt. % H	$(H/C)_T^3$	$(H/C)_{al}^4$	$(H/C)_{ar}^5$	$(f_a^C)^6$	$(f_a^H)^7$
COED-5 JP-5	87.8+7.7 ¹ (87.12) ²	13.60+1.0 ¹ (13.58) ²	1.88+0.25 (1.87)	2.14+0.3	0.49+0.08	0.158+0.008	0.043+0.00
Skale Paraho JP-5	91.3+6.0 ¹ (86.69) ²	14.38+1.4 ¹ (13.92) ²	1.87+0.08 (1.93)	2.19+0.10	0.37+0.02	0.172+0.006	0.034+0.00

Footnotes: 1) Standard deviations based on four independent measurements for both the ¹³C and ¹H FT nmr values

2) Values in () are from elemental combustion analysis

3) $(H/C)_T$ = the total hydrogen to carbon ratio

4) $(H/C)_{al}$ = the aliphatic hydrogen to carbon ratio

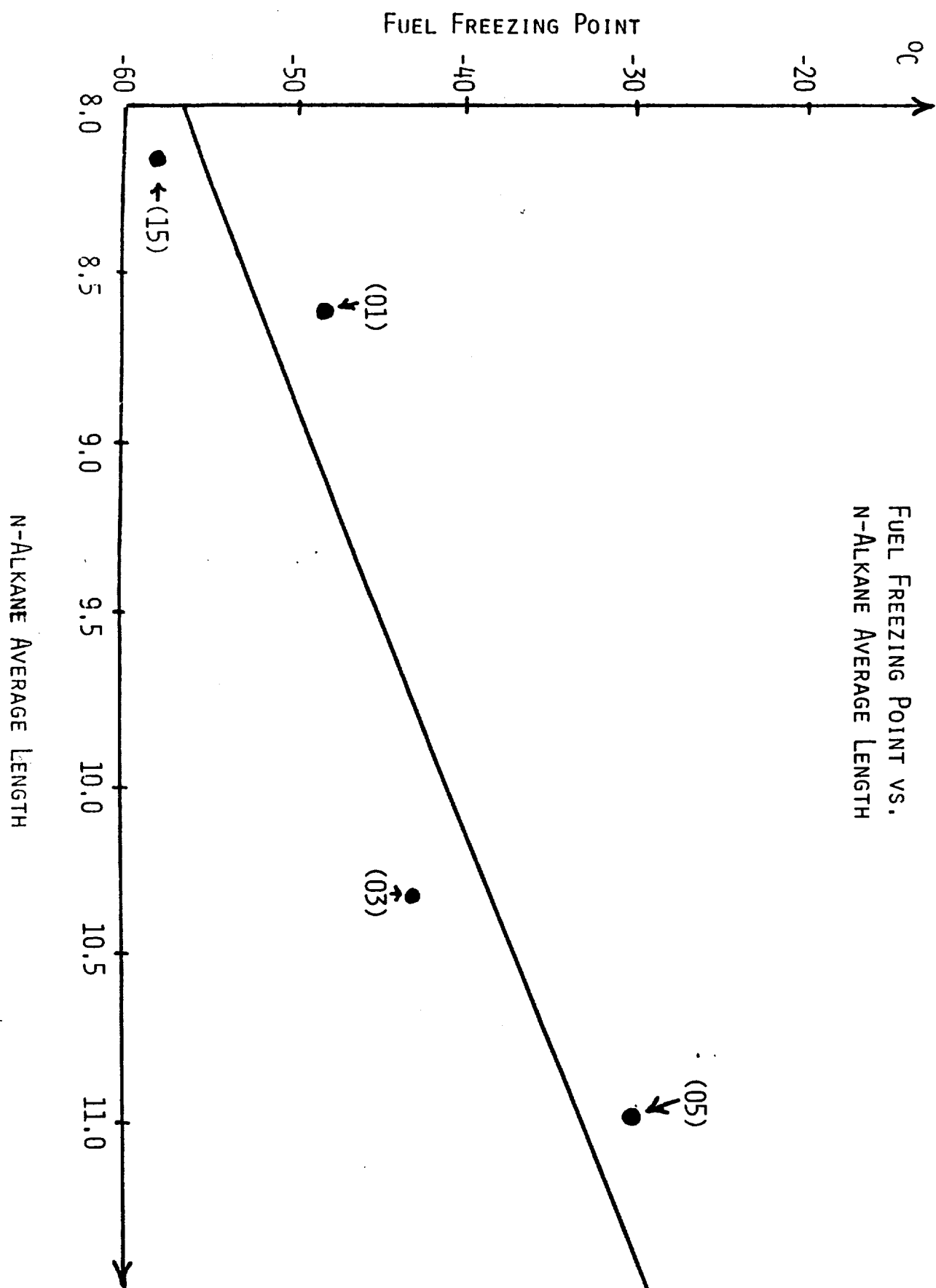
5) $(H/C)_{ar}$ = the aromatic hydrogen to carbon ratio

6) f_a^C = the aromatic carbon to total carbon ratio (aromaticity)

7) f_a^H = the aromatic hydrogen to total hydrogen ratio

FIGURE 1

FUEL FREEZING POINT VS.
N-ALKANE AVERAGE LENGTH



ANALYSIS OF JET FUELS BY MASS SPECTROMETRY

by: S. E. Buttrill, Jr.

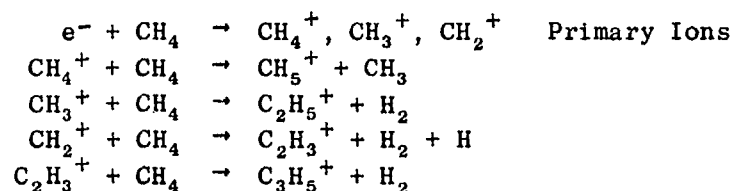
SRI International

As both the worldwide and domestic supplies of oil decrease, the nation's security requires the development of synthetic fuels derived from other sources. These materials are very complex mixtures of hundred of compounds. Basic research to improve the performance and stability of synthetic fuels could be facilitated by analytical methods giving accurate, quantitative, and precise information on the amounts of the different compounds present. This information could then be correlated with the physical and performance properties of the fuels to determine which compounds were responsible for a particular fuel characteristic. This paper describes specialized mass spectrometric techniques which can provide this type of detailed information on jet fuel composition.

Analysis by mass spectrometry involves three principal steps. First, the sample of liquid or solid is vaporized and introduced into the mass spectrometer at a pressure which is usually less than 10^{-5} torr. At this low pressure, the molecules of the sample do not interact with each other leading to the important result that the mass spectrum of a mixture is just the sum of the spectra of each of its components. Secondly, the sample molecules are converted into ions by any one of a number of processes. The most common method is to bombard the sample vapor with 70-100 eV electrons. This produces many fragment ions which, for pure samples, may be used to deduce the structure of the sample molecule, but which lead to very complex and useless spectra for unknown mixtures. Furthermore, unfragmented molecular ions may not be formed in large enough quantities to be detected. For analysis of complex mixtures, other types of ionization such as chemical ionization or field ionization are required as discussed below. Finally, the ions are separated according to mass. The relative numbers detected are recorded as a function of mass to produce the mass spectrum. The two most common mass analyzers are magnetic sectors and quadrupoles.

In chemical ionization, ions are formed from the sample by ion/molecule reactions. A reagent gas is present in the mass spectrometer ion source at a pressure of about 1.0 torr. Most often, this gas is methane. Through a series of ion/molecule

reactions, the ions initially formed from methane by electron impact react to form CH_5^+ , C_2H_5^+ , and C_3H_5^+ as shown.



These reagent ions do not react further with methane, but will react with most sample molecules to form protonated molecules of mass (MW + 1) or in the case of saturated hydrocarbons, to form ions of mass (MW - 1). The sample ions will often fragment because of the generally high exothermicity of the reaction, but usually a peak is detected in the molecular ion region, e.g., either (MW + 1) or (MW - 1). As in the case of electron impact, the presence of fragment ions greatly complicates the analysis of complex mixtures.

While it is impossible simultaneously to ionize all compounds in a mixture without fragmenting at least some of them, one can choose a chemical ionization reagent gas which is highly selective. For example, if about one percent ammonia is added to the methane, all of the methane ions will rapidly react to form NH_4^+ which now become the reagent ions. Because of the thermochemistry of the proton transfer process, NH_4^+ will protonate amines, pyridines, anilines, etc. (e.g., all nitrogen bases) but will not react with hydrocarbons, phenols, alcohols, esters, ethers, or similar compounds. This scheme provides a simple way to obtain a molecular weight profile of just the nitrogen bases present in a fuel without requiring any prior separations. All of the components of the fuel are vaporized into the mass spectrometer, but only the nitrogen compounds are ionized and detected.

Field ionization is unique among the many different ionization techniques in its ability to produce unfragmented molecular ions from most organic compounds (1). Furthermore, a recent study has shown that the relative ionization efficiencies of many different classes of compounds are very similar, ranging only over a factor of two (2). In situations where quantitation of specific compounds is required, the corrections for these small variations are easily made. When dealing with complex mixtures of unknown substances, field ionization is the method of choice for obtaining semiquantitative molecular weight profiles. SRI has three different types of field ionization sources in operating mass spectrometers and maintains a continuing program developing new designs with greater efficiency and reliability.

The mass spectrometer used for multicomponent analysis work is a 60° magnetic sector of 25-cm radius. Mass resolution is 1200 with a mass range of 0-4000. Typical overall ionization efficiency is 10^{-7} ions/molecule although efficiencies as high as 10^{-5} have recently been obtained. An ionization efficiency of 10^{-7} means that when the mass spectrometer is tuned to the molecular weight of the sample, one ion is detected for every 10^7 sample molecules introduced on the solid sample probe. If the mass spectrometer is scanning over a 700-amu range, one ion will be detected, on average, for every 2×10^{10} molecules in the sample. The factor of 2000 accounts for the ions which are formed but not detected because the mass spectrometer was at a different point in its mass scan. In other words, 0.5 ng of a compound with a molecular weight of 300 will produce a peak containing 50 ion counts, even when the compound is one of hundreds in a typical 200- μ g sample. The molecular weight profile of a sample is obtained by recording mass spectra as the sample temperature is slowly increased, and then adding up all of the spectra into a composite spectrum containing a peak at each mass corresponding to the molecular weight of one or more components of the mixture.

The field ionization mass spectrometer is interfaced to a PDP 11/10 dedicated computer (Figure 1). The computer controls the magnet scan of the mass spectrometer by means of the 12-bit digital-to-analog converter (DAC). The data acquisition program increments the input to the DAC at precisely controlled time intervals so that each channel is receiving ions counted for exactly the same amount of time.

The 12-bit analog-to-digital converter (ADC) is connected to a temperature programmer for the solids probe. At the end of each mass spectrometer scan, the temperature of the probe is recorded for later use in the printed reports or data analysis. Since the temperature programmer is digitally driven, a given temperature program can be very precisely reproduced to allow meaningful comparisons between samples. Our experience indicates that most pure compounds are volatilized over a narrow temperature range of 10-30°C. Thus, separate peaks will be observed in the temperature profile of a single mass if there is more than one component of the sample with that particular molecular weight. It is possible to distinguish between genuine low molecular weight components of a sample and those resulting from the thermal decomposition of much larger molecules because these two different types of species appear at very different temperatures. Our experiments show no indication of significant pyrolysis of coal liquefaction products or of crude oils.

A typical molecular weight profile of a coal liquid is shown in Figure 2. Additional examples of the types of information currently available from the combination of FIMS and the PDP 11/10 computer are shown in Figures 3a and 3b. The

sample was fractions 1 and 2 of basic compounds from an H-coal product and was provided to us by the Atlantic Richfield Company. The evolution of this spectrum as a function of temperature is presented in Figures 3a and 3b showing the plotted spectra integrated within the different temperature ranges during the evaporation of a single sample.

The first three spectra in Figure 3a show volatile components of the sample that came off as soon as the sample was introduced into the mass spectrometer. When the signal produced by these volatile materials began to decrease, the operator started the temperature program, heating the sample at about 2°C per minute. The heating rate was increased twice during the run to maintain a reasonably high signal as the less volatile components were being analyzed. Finally, three spectra were recorded at 325°C (Figure 3b), which was the final probe temperature for this sample. Weighing the sample before and after analysis showed that 94% of this material was volatilized.

These results illustrate the vast amount of information to be obtained by combining chemical separations with nonfragmenting FIMS.

Figure 4 is an example of a spectrum of a crude oil analyzed by the computer in the same manner as the samples presented in Figures 2 and 3. The only difference was that the crude oil sample was "weathered" in the probe at room temperature to remove the most volatile constituents. The same sample was analyzed five times to assess the variance of the analytical procedure. Figure 5 presents the standard deviation of each of the mass peaks as a function of molecular weight. One can see here that the constituents below 250 amu have a high variance due to irreproducible preevaporation ("weathering"), but in the mass range 250 to 550, the standard deviation is in the range of 3 to 6%, which is very satisfactory for such a complex analysis. It should be noted that even the most abundant constituents in our complex mixture amount to just about 0.6% of the total. At higher molecular weights, there is an increase in the variance predominantly because of the lower abundance of these constituents and possibly also because of some irreproducible polymerization of such minor components. The effect of abundance on the variability of the individual constituents can be seen in Figure 6 which also presents the theoretical lower limit of variance due to statistical fluctuations of the ions counted. The two lines "200" and "800" designate the theoretical limit for these two extreme cases of molecular weights. The limits are different because of the difference in the monitoring time per amu during the magnetic scanning. The actual variance is about 2 to 3 times higher than the theoretical lower limit. This is very satisfactory in view of the complexity of the sample and the analytical procedure.

REFERENCES

1. H. D. Beckey, Field Ionization Mass Spectrometry, Pergamon Press, Elmsford, N.Y., 1971
2. S. E. Scheppele, P. L. Grizzle, G. J. Greenwood, T. D. Marriott, and N. B. Perreira, "Determination of Field Ionization Relative Sensitivities for the Analysis of Coal-derived Liquids and Their Correlation with Low Voltage Electron Impact Relative Sensitivities," Anal. Chem. **48**, 2105 (1976).

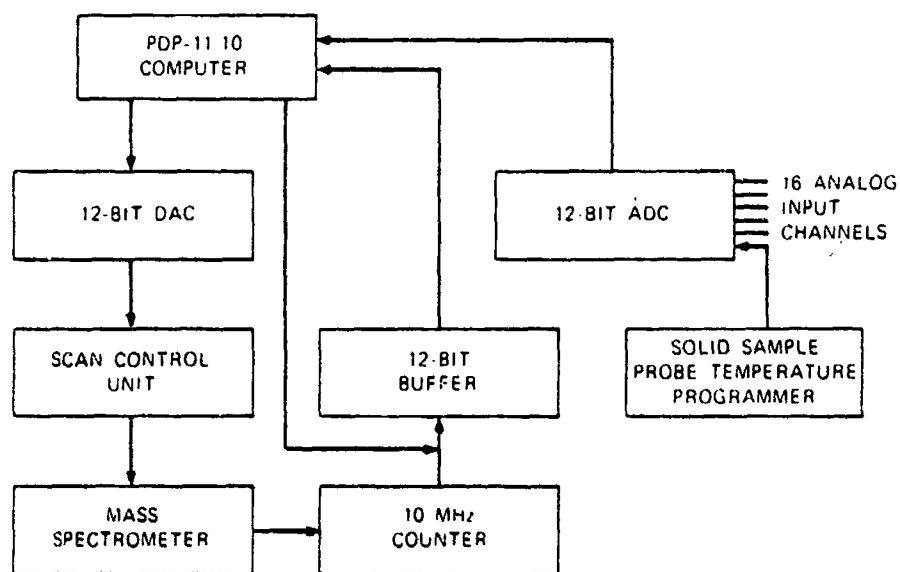


FIGURE 1 MASS SPECTROMETER-COMPUTER INTERFACE

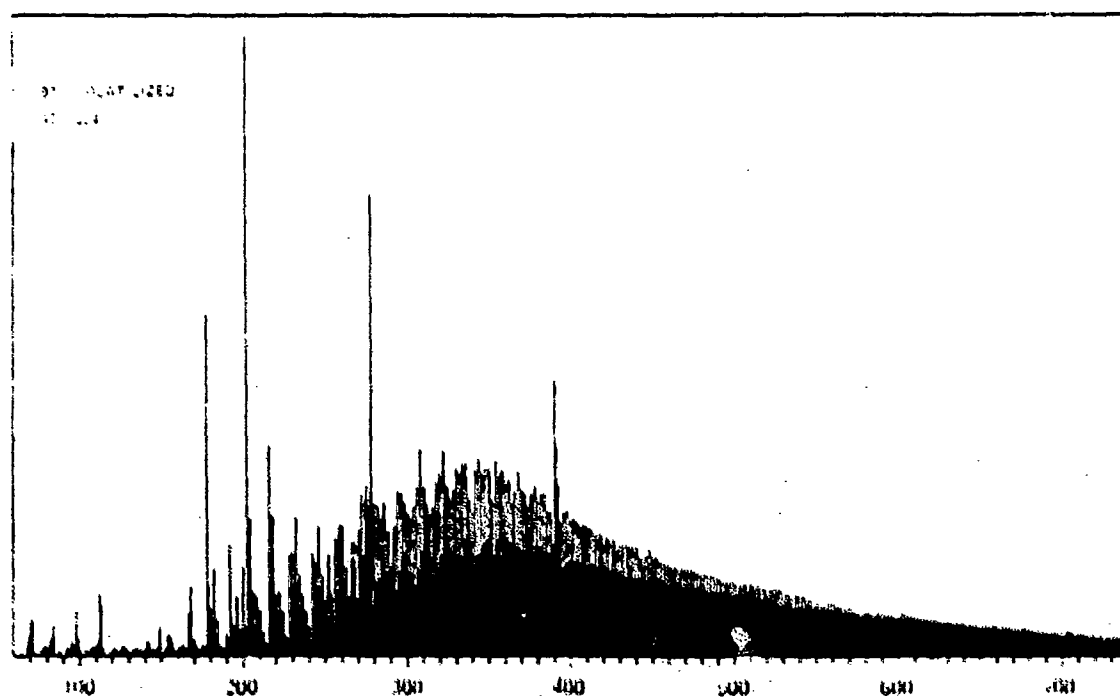


FIGURE 2 KENTUCKY 9/14 SRC. OILS FRACTION (SOURCE: ARCO)

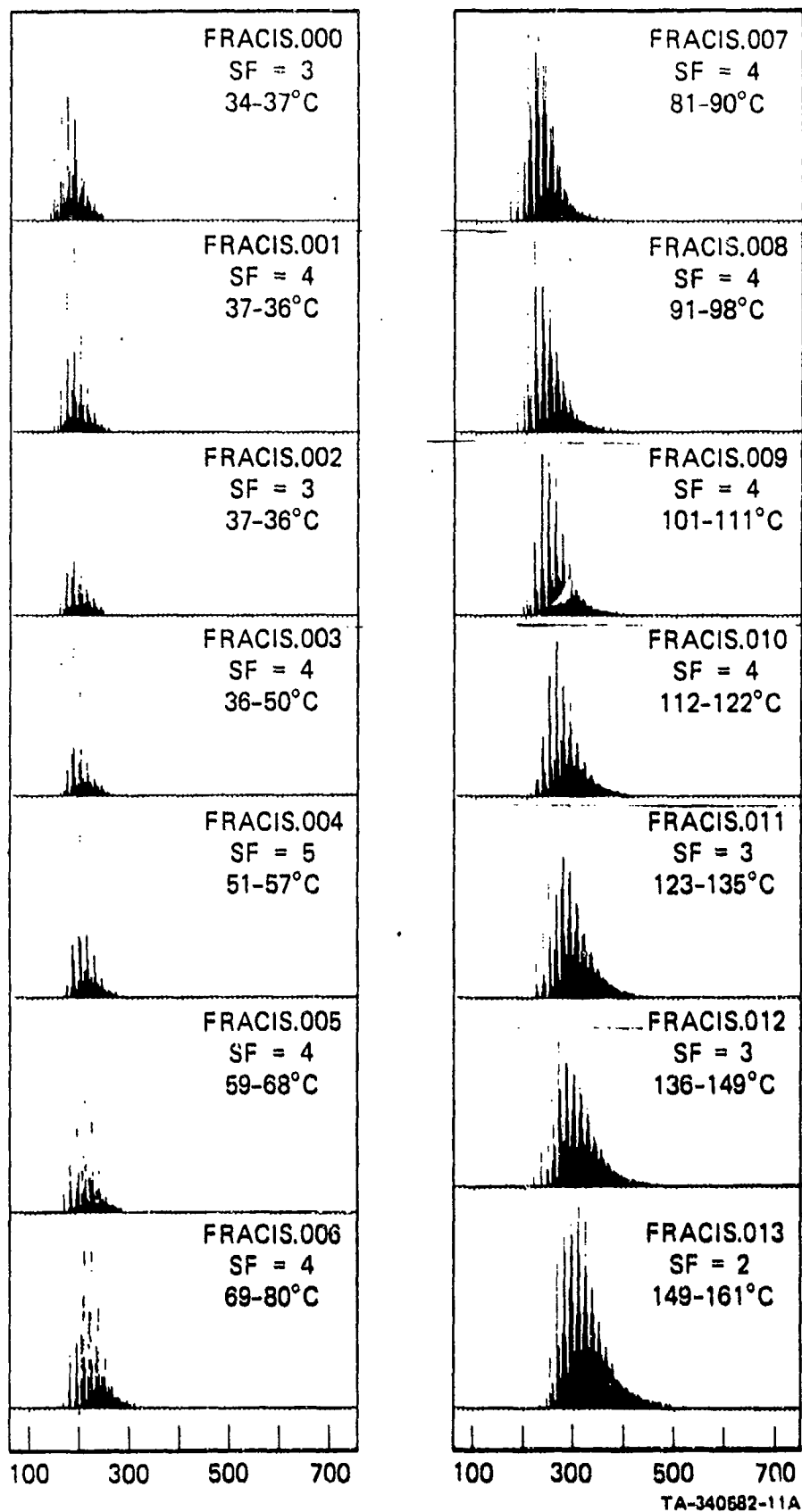


FIGURE 3A FRACTIONS 1 AND 2 FROM H-COAL PRODUCT 177-57-49 BY COLUMN CHROMATOGRAPHY (SOURCE: ARCO)

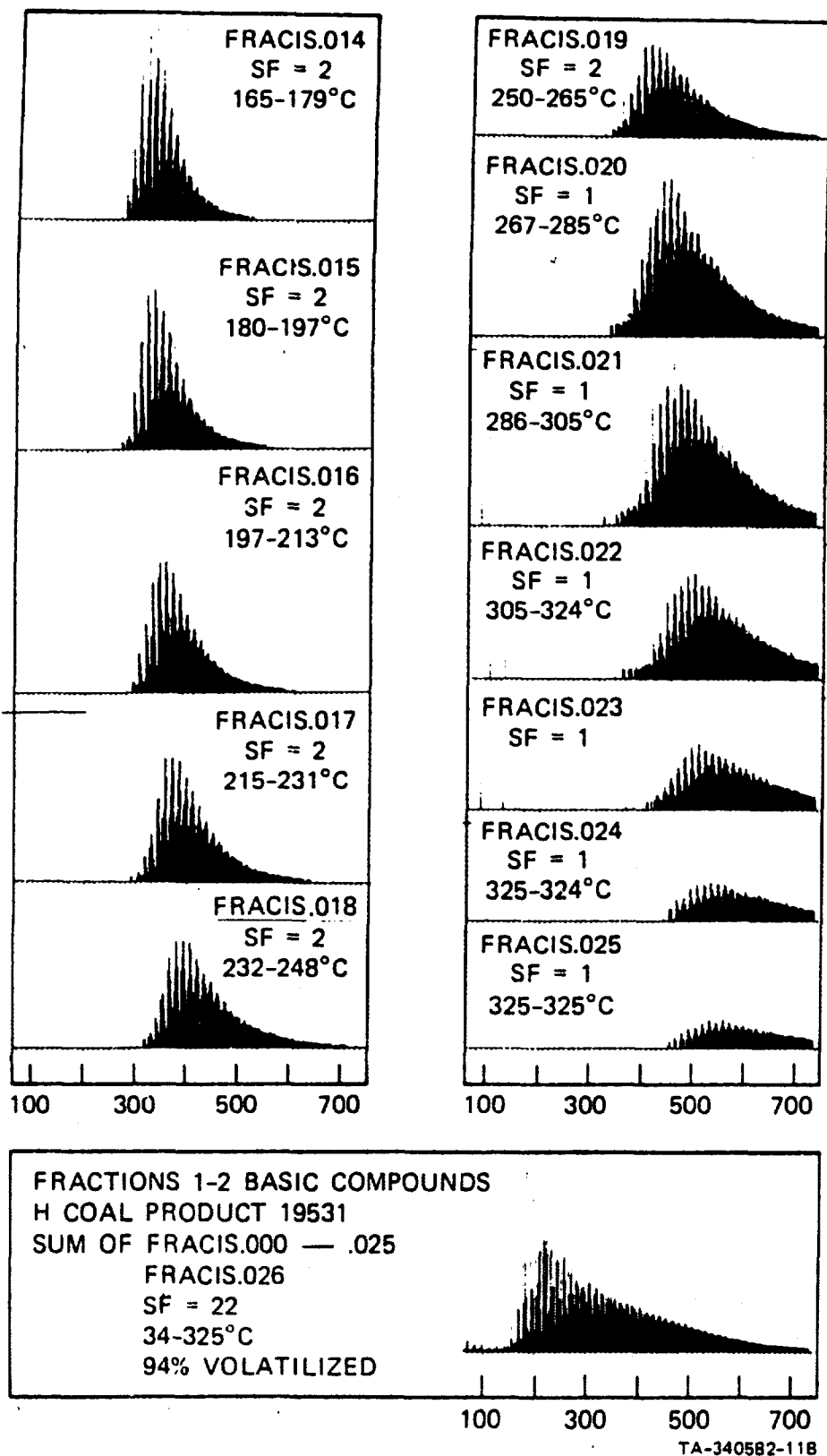
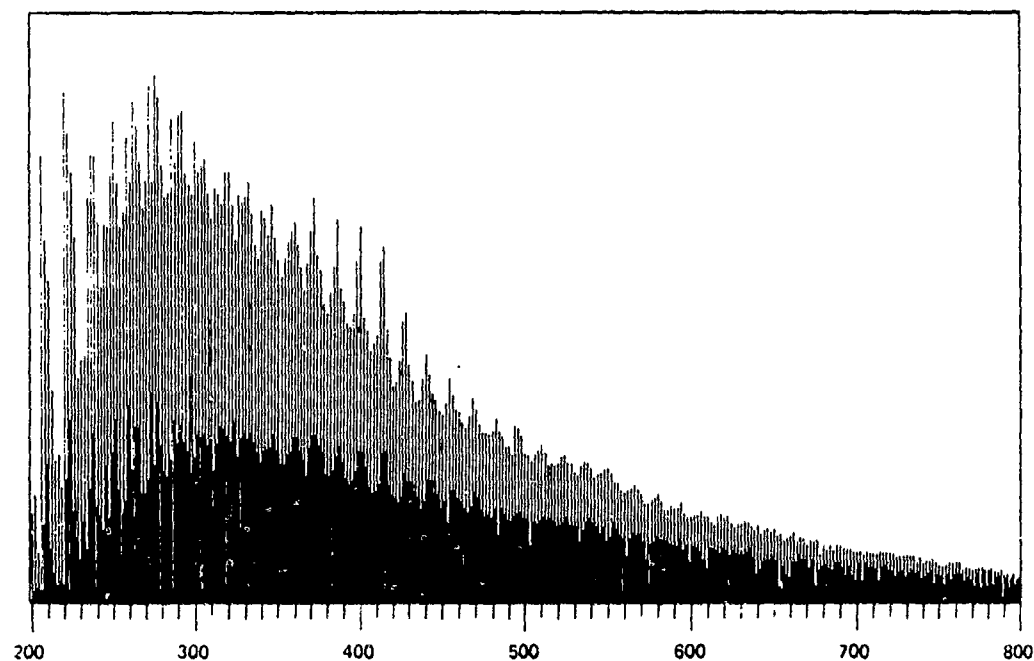
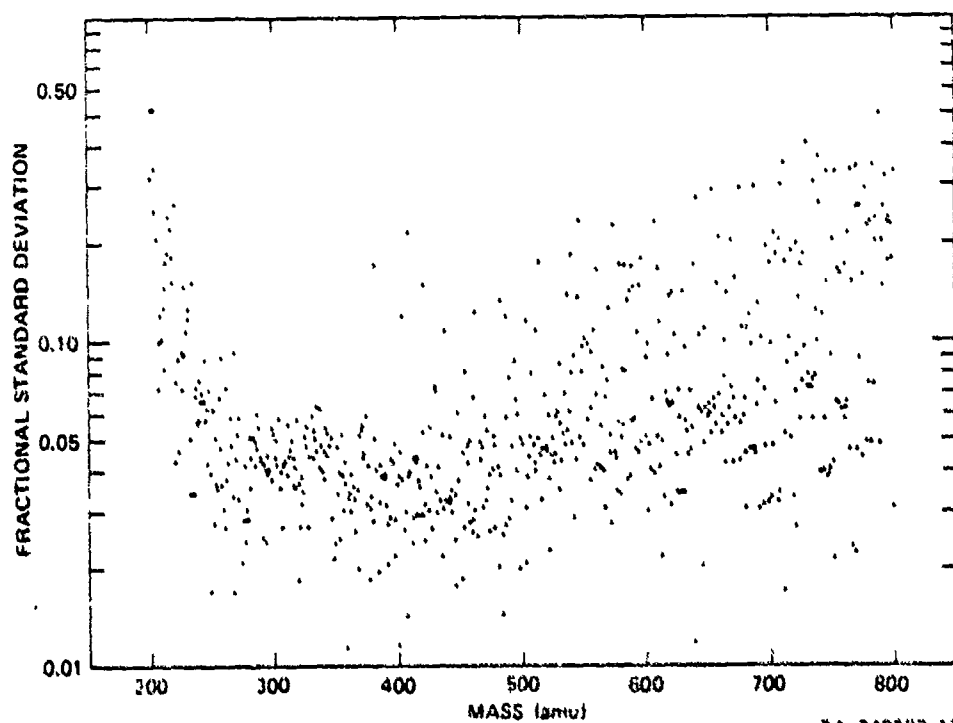


FIGURE 3B FRACTIONS 1 AND 2 FROM H-COAL PRODUCT 177-57-49 BY COLUMN CHROMATOGRAPHY (SOURCE: ARCO)



TA-340582-14

FIGURE 4 VENEZUELAN OIL WEATHERED IN MASS SPECTROMETER



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FIGURE 5 STANDARD DEVIATION OF EACH OF THE MASS PEAKS AS A FUNCTION OF MOLECULAR WEIGHT

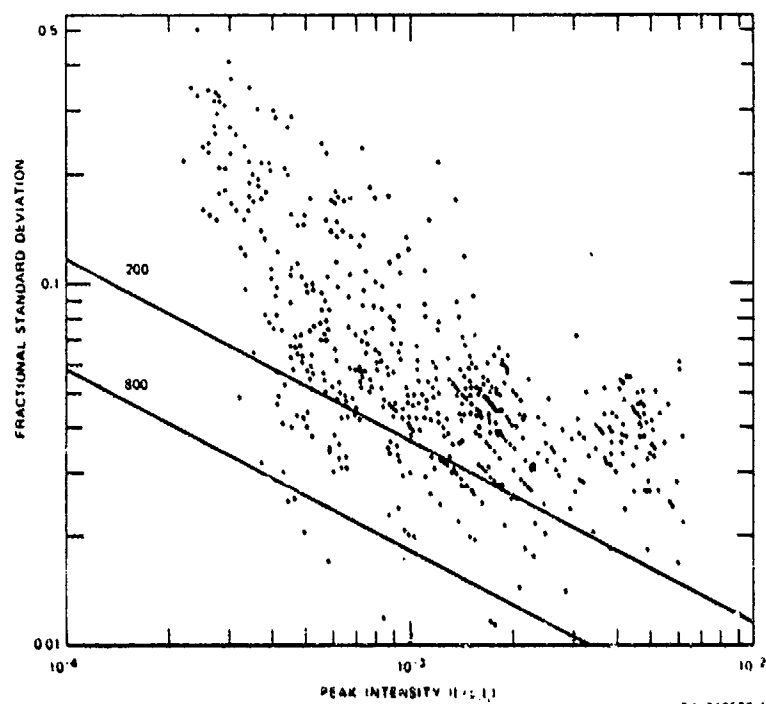


FIGURE 6 EFFECT OF ABUNDANCE ON VARIABILITY OF INDIVIDUAL CONSTITUENTS

EVALUATION OF COMPARATIVE TOXICITY AND SHIPBOARD
HAZARDS OF SELECTED PETROLEUM AND OIL SHALE DERIVED FUELS

BY: LCDR L. E. Doptis

Naval Medical Research & Development Command

SUMMARY

Since the initiation of Project INDEPENDENCE, the Navy has been active in the production of shale oil crude by surface retorting, as well as the refining of crude shale oil into product fuels for military use. Information on the health effects of these product fuels are necessary in order to determine the adequacy of engineering controls limiting exposures of personnel using fuels, and for the formulation of safe work procedures in naval shipboard and shore facilities. Naval activities to identify health effects associated with selected shale oil fuels, in comparison with their petroleum-derived analogs, and to characterize fuel exposures of personnel are described.

A review of world-recoverable fossil fuels, in comparison to U.S. recoverable reserves and consumption patterns, suggests that the U.S. is facing an energy crisis^{1,2} similar to that of 16th century Britain³, when coal became a widespread substitute for a depleted fuel source--the forests. Fortunately the U.S. possesses substantial coal and oil shale deposits⁴ which may supplement reserves of petroleum as sources of liquid fuel products.

The Navy's principal interest in fuels derived from non-petroleum fossil fuel sources, or synthetic fuels, is to determine their compatibility with naval equipment and engines, and their suitability as naval fuels.⁵ Past Navy involvement with synthetic fuels has included the use of coal-derived fuels in the USS JOHNSTON in 1972, and the production and refining of 10,000 barrels of Paraho crude shale oil in 1974.^{2,4} While product fuels obtained from the earlier refining of crude shale oil did not meet all military and Federal specification requirements--due to fuel instability, and the presence of wax, gum, and particulate matter, the project did demonstrate the feasibility of obtaining useful fuels from crude shale oil.^{2,5,7}

Current interest in synthetic fuels remains focused on crude shale oil from surface retorting, and the Navy is participating in an interagency effort to produce and refine larger quantities of crude shale oil into Military Specification fuels for subsequent test and evaluation.¹ It is anticipated that the use of these larger quantities of crude and an improved refining process will produce acceptable fuel products in at least six fuel fractions: JET-A, JP-4, JP-5, JP-8, diesel fuel, marine (DFM),

and a residual fuel.^{2,8}

In order to assess the suitability of shale-derived JP-5, Diesel Fuel Marine (DFM), and residual fuel to be used by the Navy, it is important that both the toxicity of the fuels and typical fuel exposures which may occur during its naval distribution and use be characterized. Comparative data on the toxicity and hazards of the synthetic and petroleum fuels are also desirable to assess the suitability of an alternative fuel, and the adequacy of existing engineering controls and work procedures. Unfortunately, little data has been available on the dermal, ocular, or inhalation toxicity of the distillate fuels used by the Navy; thus precluding a comparative evaluation of the fuels. The lack of such data has prompted many current research activities in this area, as well as recommendations for research by the National Institute of Occupational Safety and Health (NIOSH).⁹

Fuels resulting from the current shale oil production and refining program may include full-scale, shipboard demonstration tests. The early availability of data on the comparative toxicity and shipboard hazards of naval fuels is desirable, and has led to the initial evaluation of selected fuel materials as a comparative baseline for future investigations with shale-derived product fuels. The following summary will provide an overview of current research in these areas, which is particularly responsive to questions related to biological effects following low-level, long-duration exposures.

MATERIALS

JP-5. JP-5 is a high flash point aviation fuel with a specified distillation temperature of 205°C (10% point) to 290°C (endpoint).¹⁰ Specifications permit up to 25% aromatic hydrocarbons and 5% olefins. Phenols or amines are added to inhibit oxidation. The fuel is a complex, kerosene-type mixture that can contain higher boiling components than specified by Military Specification.¹¹

Diesel Fuel Marine. Diesel Fuel Marine (DFM) is also a distillate fuel, with a specified boiling range lower than 385°C.¹² The content of aromatics and olefins is not specified, but is limited by the requirement that the fuel be clear and bright in appearance.

The following paragraphs will describe investigations employing these materials up to the present time.

METHODS

Personnel exposures to these fuels are being characterized by thorough industrial hygiene evaluation of ships expected to be characteristic of the Navy in the 1980's and beyond. A principal objective of the study is to quantify both atmospheric contaminants and fuel exposures associated with fuel use. Both personal (breathing zone) and general area samples for total and respirable particulate, combustion products, and hydrocarbon

vapors are being collected and analyzed by a variety of methods, which include adsorption of hydrocarbons with subsequent analysis by gas chromatography--mass spectroscopy. Jobs and occupations involving fuels are also being identified, along with exposure durations and an assessment of the potential for intermittent or prolonged skin contact with the fuels.

Until 1976 when Knave and co-workers¹³ reported signs of polyneuropathy in Swedish aircraft workers chronically exposed to jet fuel vapors, the vapors of aliphatic hydrocarbons were generally reported to produce few harmful effects, even for prolonged exposures. Coincidentally, a phased, behavioral toxicological evaluation of these materials, illustrated in Figure 1, had already been initiated on naval fuels. Phase 1 is a general behavioral screen, in which spontaneous home-cage activity, food and water consumption, weight, and behavioral profiles of individual rats are observed after acute dosing. This phase of investigation serves to identify the range of doses that can produce gross toxic effects, as compared to those that produce no detectable behavioral signs of toxicity. In Phase 2, a battery of tests is used to define the specific type of behavior affected, and consists of specific tests for changes in visual function, peripheral sensitivity, aggression, and motor integration. Subsequent iteration of the screening procedures involves more detailed evaluation of affected behaviors, and definition of dose and time effect relationships.

Prior to the behavioral experiments, a series of inhalation investigations was initiated to assess the inherent toxicity of

military grade JP-5. The experimental design of the first study, initiated in December 1974, is shown in Table 1. A high-concentration of JP-5 vapor (643 mg/m^3) was selected to maximize the likelihood of observing effects due to the exposure. Fuel vapors were generated by bubbling air through the JP-5 and into a two cubic meter Rochester-type inhalation chamber. The JP-5 used for vaporization was changed every 12 hours, and the chamber concentration was sampled every 15 minutes and monitored as total hydrocarbons. More recently, an experiment designed to extend this earlier work on JP-5 and to provide data to serve as a basis for comparison of oil shale-derived JP-5 has been initiated at the Naval Medical Research Institute (NMRI) Toxicology Detachment at Wright-Patterson Air Force Base, utilizing Thomas-Domes at the USAF Aerospace Medical Research Laboratory/Toxic Hazards Research Unit. JP-5 vapors were generated for this study by passing JP-5 through a column heated to 120°F , exposure concentrations were established for 750 mg/m^3 and 180 mg/m^3 , Table 2. Two-thirds of the male and female rats are presently being held for, approximately, their normal lifetime. At that time, 42 tissues will be submitted for histopathologic evaluation of the 90-day continuous exposure to petroleum JP-5.

Three inhalation exposure experiments with DFM have been conducted in the last five years, with essentially the same objectives and designs as the previously discussed JP-5 studies. The first experiment utilized a two cubic meter Rochester chamber, Table 3, with a total chamber hydrocarbon vapor concentration of 14 mg/m^3 chosen to assess inhalation exposures to low levels of

of petroleum-derived DFM. Twenty-four of the exposed and control rats were held for approximately two years for histopathologic evaluation. A second inhalation experiment was conducted with a vapor and aerosol. The chamber concentration was maintained at 167 mg/m³ total hydrocarbons for a duration of 120 days in an attempt to obtain an effect which could serve as a benchmark for further observations, Table 4. As in the previous experiment, 24 rats were held for approximately two years in order to assess the long-term effects of 120-day continuous inhalation exposure to petroleum DFM. A third experiment, with essentially the same designs and objectives as the more recent JP-5 experiment, has been initiated at the NMRI Toxicology Detachment as a baseline for comparative evaluation of shale-derived DFM, Table 5. The concentration of 300 mg/m³ represents the highest vapor concentration that can be produced without creating an aerosol.

RESULTS

The following are preliminary findings of the previously discussed studies.

As regards the characterization of existing fuel exposures of personnel, small quantities of organic vapors, respirable particulates including oil mist, and small quantities of polycyclic aromatic hydrocarbons have been detected. The study is approximately 60% complete, and shipboard investigations are expected to be completed by 1 October 1978.

With respect to the animal toxicology of selected fuels, there are more indications of neurobehavioral effects in the animals dosed with the petroleum-derived JP-5 despite more pronounced signs of gross toxicity in animals dosed with DFM.

As illustrated in the comparison of spontaneous home-cage activity, Figure 2, animals dosed with JP-5 exhibited very significant increases in activity on the day after exposure, followed by a significant depression in activity from the fourth day of testing; no significant effect was observed for animals similarly dosed with DFM. Additionally, the JP-5 animals have been observed to be much more aggressive after dosing than DFM-dosed animals. These observations, together with observations of heightened sensitivity to touch in the JP-5-dosed animals, suggest that JP-5 is the more behaviorally active of the two materials following oral administration.

In addition to the comparison of petroleum-derived DFM with JP-5, a preliminary comparison of a petroleum-derived JP-5 (with two different shale-derived JP-5's) is shown in Table 6. The JP-5 fuel derived from shale and refined by the Gary-Western process (Shale A) was significantly more toxic than other JP-5 fuels which were studied. The LD_{50/14} for the Gary-Western JP-5 was approximately 26 ml/kg, whereas the other shale-derived product did not produce any deaths within 14 days. It is known that differences exist in the chemical characteristics of these materials; however, it is not known with certainty which causative factor(s) produced differences in the observed toxicity. Table 7 illustrates some of the chemical and physical properties of JP-5 materials available to the Navy. The

observed differences in toxicity may be the result of the high nitrogen content present within the Gary-Western fuel (Shale A), Table 8, or other characteristics as yet unidentified.

Turning to investigations with inhalation exposures of the fuels, the results of the hematologic and histopathologic examinations are considered unremarkable for all experimental species, and no deaths are attributable to the fuel exposures. These exposures suggest a low order of toxicity for the fuels; however, these data are incomplete since tissues are being reviewed by veterinary pathologists at this time.

DISCUSSION

Few data have been available to assess the inherent toxicity of product fuels derived from petroleum, with the exception of earlier investigations related to the chronic toxicity of JP-5 jet fuel. Based upon data from these JP-5 investigations, it was suggested that workmen should not be occupationally exposed, i.e., intermittently for eight hours a day, five days per week, to more than 2.5 mg/l of JP-5 vapors. Anticipating that the Navy would utilize oil shale-derived fuels prior to their widespread commercialization, questions arose related to chronic health effects possibly related to low-level, long-term exposures of personnel to higher boiling point distillate fuels, particularly those derived from shale.^{14, 15} These previously described studies, along with other coordination activities, were initiated to assure the availability of adequate health criteria information on product fuels of principal interest to the Navy.^{3, 16, 17, 18}

It is anticipated that the current efforts of the Navy and other agencies will provide substantial information on the toxicity of oil shale materials, a comparative data base on petroleum materials, and timely availability of toxicological and industrial hygiene information to assure the safe use and handling of shale oil product fuels.

ACKNOWLEDGMENT

I wish to thank Robert N. Hazlett for his technical assistance with the analyses of fuel samples.

REFERENCES

¹ Energy Fact Book 1975, U.S. Navy Energy and Natural Resources Research and Development Office, Washington, DC, ONR Contract #N00014-74-C-0348, Tetra Tech, Inc., 1911 North Fort Myer Drive, Arlington, VA 22209.

² "Sixth Synthetic Fuels Coordination Meeting," 15 December 1976, U.S. Navy Energy and Natural Resources Research and Development Office, Washington, DC.

³ Nef, John U. Scientific American, Vol. 237, No. 5, November 1977.

⁴ Final Report: The Production and Refining of Crude Shale Oil into Military Fuels, ONR Contract #N00014-75-C-0055, Applied Systems Corporation, Vienna, VA, August 1975.

⁵ U.S. Navy Energy R&D Progress: April-September 1976, U.S. Navy Energy and Natural Resources Research and Development Office, Washington, DC, November 1976.

⁶ Compilation of Oil Shale Test Results, ONR Contract #N00014-76-C-0427, Applied Systems Corporation, Vienna, VA, April 1976.

⁷ The Production and Refining of 10,000 Barrels of Crude Shale Oil into Military Fuels, ONR Contract #N00014-75-C-0055, U.S. Navy Energy and Natural Resources Research and Development Office, Washington, DC, Applied Systems Corporation, Vienna, VA, June 1975.

⁸ Roberts, Alan. "Overview of Navy Energy R&D Program Related to the Production and Refining of 100,000 Barrels of Shale Oil," Synthetic Fuels Interagency Coordination Meeting, 19-20 July 1977, Wright-Patterson AFB, Dayton, OH.

⁹ Criteria for a Recommended Standard--Occupational Exposure to Refined Petroleum Solvents, U.S. Department of Health, Education and Welfare, National Institute of Occupational Safety and Health, U.S. Government Printing Office, Washington, DC, July 1977.

¹⁰ Military Specification 1965: Turbine Fuel, Aviation Grades JP-4 and JP-5, MIL-T-5624K, 18 pp.

¹¹ Annual Report of Research: November 1976-31 October 1977, "Environmental Toxicology of Naval Fuels and Ordnance Compounds," Naval Biosciences Laboratory, Oakland, CA, March 1978.

¹² Military Specification 1965: Fuel, Oil, Diesel, Marine, MIL-F-16884F, 5 pp., 1976.

¹³ Knave, B., H.E. Persson, J.M. Goldberg, and P. Westerholm. "Long-Term Exposure to Jet Fuel: An Investigation on Occupationally Exposed Workers with Special Reference to the Nervous System," Scandinavian Journal of Work Environment and Health, Vol. 3, pp. 152-164, 1976.

¹⁴ Hazardous Chemicals in Raw and Upgraded Shale Oil, Workshop on the Health Effects of Coal and Oil Shale Mining, Conversion and Utilization, University of Cincinnati, Cincinnati, OH, 27-29 January 1975 (Standard Oil Company (Indiana), 910 S. Michigan Avenue, Chicago, IL 60605).

¹⁵Hueper, W.C. "Experimental Studies on Cancerigenesis of Synthetic Liquid Fuels and Petroleum Substitutes," AMA Archives of Industrial Hygiene, Vol. 8, pp. 307-327, October 1953.

¹⁶Doptis, L.E. "Navy Concerns Related to Health Effects of Oil Shale and Synthetic Fuels," U.S. Environmental Protection Agency Advanced Fossil Fuels Sector Group Meeting, Cincinnati, OH, 31 March 1976, EPA Meeting Report: EPA-600/7-76-001, June 1976.

¹⁷Proceedings of the 5th Annual Conference on Environmental Toxicology: 24-26 September 1974, USAF AMRL-TR-74-125, Aerospace Medical Research Laboratory, Aerospace Medical Division, Air Force Systems Command, Wright-Patterson AFB, December 1974.

¹⁸"Interagency Ad Hoc Committee on the Health Effects of Converted Hydrocarbon Fuels," Committee on Toxicology, National Academy of Sciences/National Research Council, 1975.

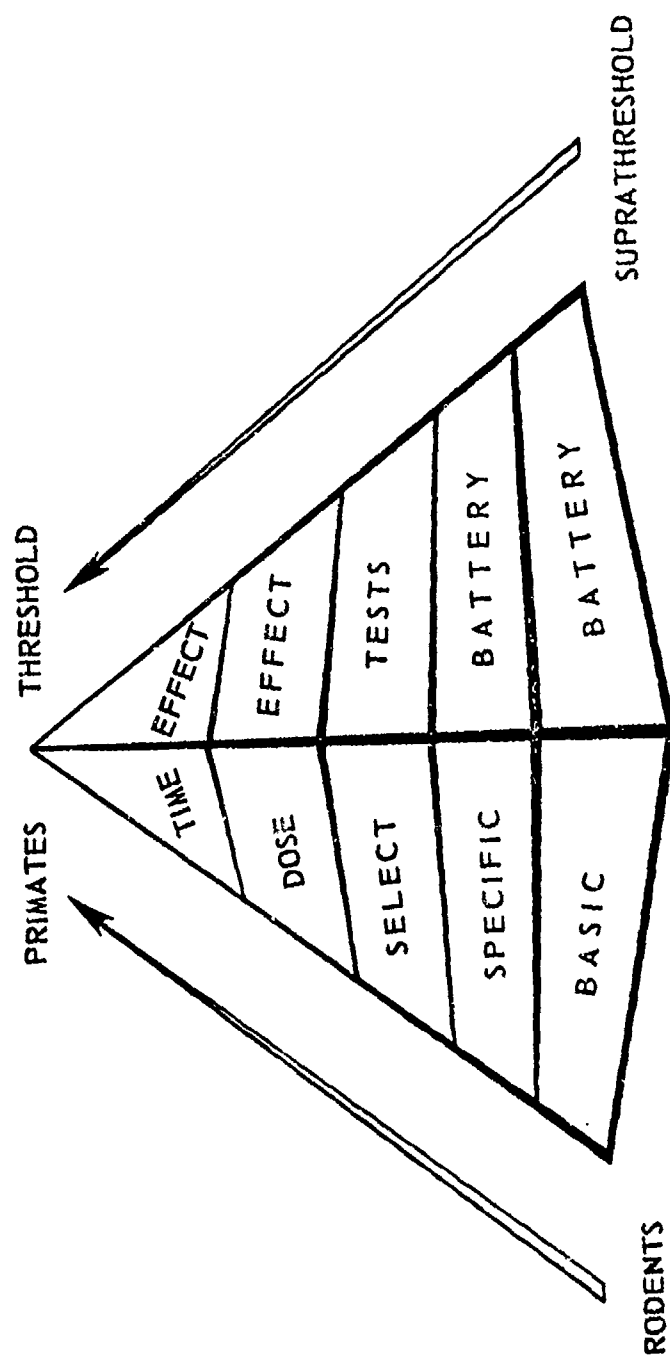
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JP-5 CONTINUOUS EXPOSURE

Laboratory:	NMRI
Test Material:	Military Specification JP-5
Concentration:	643 mg/m ³ total hydrocarbons (vapor)
Duration:	120 days (23 hours/day)
Animal Compliment:	Rat 15 Guinea Pig 15
Clinical Tests:	Body Weight, Hematocrit, Hemoglobin, WBC
Histopathology:	Lung, Liver, Heart, Kidney, Spleen

TABLE 1

JP-5 CONTINUOUS EXPOSURE

Laboratory:	NMRL/AMRL/THRU
Test Material:	Military Specification JP-5
Concentrations:	750 mg/m ³ and 180 mg/m ³ total hydrocarbons (vaporizing below 120°F)
Duration:	90 days
Animal Complement:	(at each concentration) Rats 75 male and 75 female (50 of each being held for 2 years) Mice 150 female Dogs 3 male and 3 female
Clinical Tests:	Body Weight, Hematocrit, Hemoglobin, RBC, WBC, RBC Indices, Sodium, Potassium, Calcium, Serum Proteins, Glucose, Alkaline Phosphatase, SGOT, SCPT, Bilirubin, Creatinine, BUN
Histopathology:	90 days - 42 tissues 2 years - 42 tissues

TABLE 2

DFM CONTINUOUS EXPOSURE

Laboratory:	NMRI
Test Material:	Military Specification DFM
Concentration:	14 mg/m ³ total hydrocarbons (vapor)
Duration:	90 days (23 hours/day)
Animal Compliment:	Rats 42 (24 held for 2 years) Guinea Pigs 42
Clinical Tests:	Body Weight, Hematocrit, Hemoglobin, WBC
Histopathology:	90 days - Lung, Liver, Heart, Kidney, Spleen 2 years - 42 tissues

TABLE 3

DFM CONTINUOUS EXPOSURE

Laboratory:	NMRI
Test Material:	Military Specification DFM
Concentration:	167 mg/m ³ total hydrocarbons (aerosol & vapor)
Duration:	120 days (23 hours/day)
Animal Complement:	Rats 48 (24 held for 2 years) Guinea Pigs 24
Clinical Tests:	Body Weight, Hematocrit, Hemoglobin, WBC
Histopathology:	120 days - Lung, Liver, Heart, Kidney, Spleen 2 years - 42 tissues

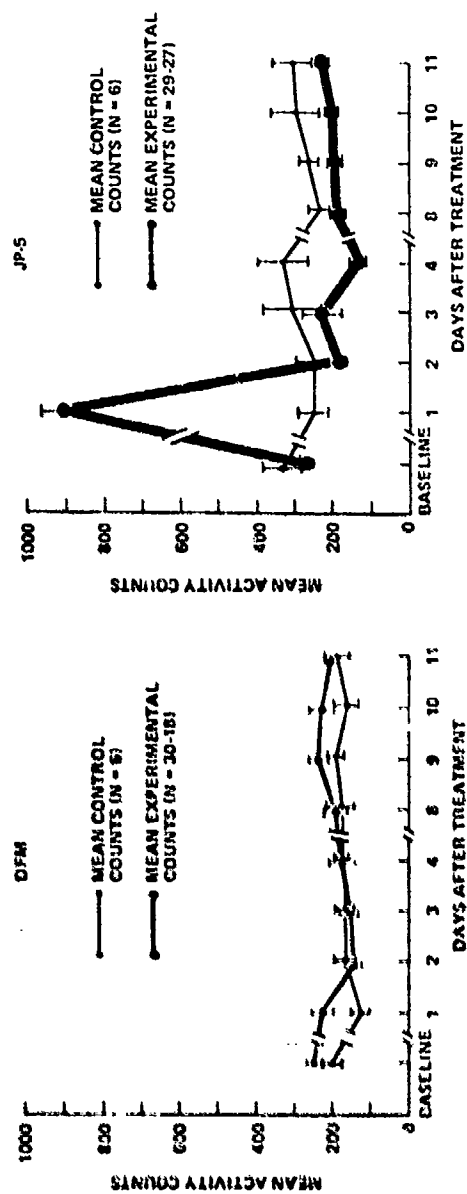
TABLE 4

DFM CONTINUOUS EXPOSURE

Laboratory:	MMRI/AMRL/THRU
Test Material:	Military Specification DFM
Concentrations:	300 mg/m ³ and 50 mg/m ³ total hydrocarbons (vaporizing below 120°F)
Duration:	90 days
Animal Complement:	(at each concentration) Rats 75 male and 75 female (50 of each being held for 2 years) Mice 150 female Dogs 3 male and 3 female
Clinical Tests:	Body Weight, Hematocrit, Hemoglobin, RBC, WBC, REC Indices, Sodium, Potassium, Calcium, Serum Proteins, Glucose, Alkaline Phosphatase, SGOT, SGPT, Bilirubin, Creatinine, BUN
Histopathology:	90 days - 42 tissues 2 years - 42 tissues

TABLE 5

LCDR L. E. DOPTIS, MSC, USN
FIGURE 2



ACUTE JP-5 TOXICITY FOR ORALLY DOSED SPRAGUE-DAWLEY RATS

DOSE GROUP (ml/kg)	% OF BODY WEIGHT	NO. OF SUBJECTS	DEATHS (14 DAYS)	
			PETROLEUM	SHALE <u>A</u> <u>B</u>
48	5	6	0	6 0
38	4	6	0	6 0
30	3	6	0	5 0
24	2	6	0	2 0

TABLE 6

JET FUEL PROPERTIES

JP-5 SPEC.

PETROLEUM

SHALE B

SHALE A

AROMATICS (VOL. %)	26.0	12.9	18.4	25.0
OLEFINS (VOL. %)	2.3	1.1	0.8	5.0
TOTAL SULFUR (WT. %)	0.05	0.032	0.05	0.4
MERCAPTAN SULFUR (WT. %)	<0.0002	-	-	0.0001
TOTAL NITROGEN (mg/l)	1,045	3.9	0.4	-
TOTAL ACID (mg KOH/g)	0.047	-	0.004	0.015
SP. GRAV. (60/60)	0.806	0.796	0.813	0.788-0.845
DISTILLATION				
IBP	340	354	348	-
5/10	366/376	375/388	376/384	- /400 max
20/30	390/402	401/412	391/400	-
40/50	414/426	422/431	410/418	-
60/70	438/452	442/455	427/437	-
80/90	468/490	470/489	448/466	-
95/EPT	510/540	504/514	480/490	- /555 max

ADDITIVES

Icing Inhibitor (Vol. %)	0.004	-	0.11	0.10-0.15
Anti-oxidant (mg/l)	-	-	-	up to 24.0 allowed
Metal Deactivator (mg/l)	-	-	-	up to 5.8 allowed
Corrosion Inhibitor (mg/l)	-	-	-	restricted

TABLE 7

NITROGEN COMPOUNDS IDENTIFIED BY GC-MS ANALYSIS
IN PARAHIO PROCESS SHALE OIL JET FUEL

	TOTAL NUMBER OF CARBONS IN SIDE CHAINS										
	0	1	2	3	4	5	6	7	8	9	10
PYRIDINES	-	-	+	++	++++	++++	+++	++	++	+	-
QUINOLINES	+	++	++	++	++	-	-	-	-	-	-
TETRAHYDROQUINOLINES	-	-	+	+	+	-	-	-	-	-	-
PYRROLES	-	++	++	-	-	-	-	-	-	-	-
INDOLES	-	-	++	++	++	++	-	-	-	-	-

+? Trace Amounts

TABLE 8

MICROBIOLOGICAL STUDIES OF JET FUELS

by: Rex Neihof

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INTRODUCTION

In the past the Navy has encountered serious problems arising from the growth of microorganisms in tanks containing hydrocarbon fuels. Such contamination generates particulate matter, emulsified water, sludges and fuel-soluble sulfur compounds which foul filters, orifices and instruments and accelerate corrosion. Water is necessary for the proliferation of microorganisms and in fuel storage facilities it may be present as condensate resulting from a decrease in fuel temperature or as seawater added to shipboard tanks as ballast. The original source of microbial contaminants may be soil or seawater. The increasing use of fuels from alternate sources may be accompanied by differences in the frequency and amount of microbial contamination of fuel/water systems because of the compositional differences between conventional and synthetic fuels. The generally higher nitrogen content of synfuels and higher n-alkane content of fuel from shale, for example, may favor microbial growth. The objective of this investigation is to determine the susceptibility to microbial contamination of jet fuels from coal and shale relative to conventional petroleum derived fuel.

PROCEDURE

Two-phase test units consisting of 50 ml each of fuel and a fresh or sea water medium with microbial inocula were set up in duplicate in different combinations as summarized in Table 1. JP-5 type fuels from coal (COED 5), oil shale (PARAHO) and petroleum and 25% mixtures of each of the synfuels with conventional JP-5 were used. For the initial tests the microorganisms used for inoculation were all obtained from field samples of infected JP-5 or diesel fuel storage tanks. They included a yeast (Candida sp.), a marine bacterium (Pseudomonas sp.), a non-mat-forming fungus (Fusarium sp.), and four species of a common mat-forming fungus (Cladosporium sp.). Appropriate controls were also included. Growth in the test units was assessed by visual inspection and by subculture on agar plates with favorable nutrient media.

RESULTS

Table 2 shows an abridged version of some of the results which serve to illustrate certain of the findings made so far. In a number of instances organisms which grew well with conventional JP-5 grew poorly with fuel from coal and even less well with fuel from shale. However, in many cases 25% mixtures of the synfuels in JP-5 were as favorable for microbial growth as JP-5 alone. Cladosporium resinae #1 and Candida are examples of this. Shale-derived fuel tends to be the most inhibitory in these cases. The bacterium, Pseudomonas marina, survives and shows slight growth in all fuels while the fungus, Fusarium, can grow well in all.

The major part of the work done thus far has been with microorganisms derived from infected tanks in which conventional fuels were stored. Additional incubation time will be required before definite conclusions can be drawn but, thus far, it appears that these organisms are not favored by the presence of fuels from shale or oil. It may be, however, that other genera, species or strains of microorganisms among the many which find their way into fuel systems may be favored by synthetic fuels. Accordingly additional microbiological collections have been made from sources deemed likely to harbor fuel-tolerant organisms. Cladosporium resinae #6 is a fungus isolated from a creosoted piling in Chesapeake Bay. In contrast to the Cladosporia isolated from conventional fuels systems it grows well with fuel from shale (Table 1).

FUTURE PLANS

Additional collections of microbial material from natural soil and water sources will be made and examined for organisms which will proliferate under synfuels. Should any be found, an effort will be made to determine what constituents of the synfuels are responsible for supporting such growth. This information will serve as a basis for recommendations to reduce the possible future hazard of microbial contamination of these fuels.

TABLE 1
MICROBIAL DETERIORATION OF SYNTHETIC FUELS

PROCEDURE: TWO-PHASE TEST UNITS*

FUEL SOURCE	WATER	MICROORGANISMS
PETROLEUM	SEA WATER	5 FUNGI
COAL	FRESH WATER	1 YEAST
OIL SHALE		1 BACTERIUM
75% PETROLEUM 25% COAL		
75% PETROLEUM 25% OIL SHALE		

*SET UP IN DIFFERENT COMBINATIONS IN 133 DUPLICATE FLASKS.

TABLE 2

MICROBIAL DETERIORATION OF SYNTHETIC FUELS. ABRIDGED RESULTS.

ORGANISM	SOURCE	AQUEOUS MEDIUM	* GROWTH			
			FUEL			
			JP-5	COAL	SHALE	25% COAL 25% SHALE
<u>CLADOSPORIUM</u> R. #1	INFECTED CONVENTIONAL FUEL TANKS	FRESH WATER	4+	±	±	4+
<u>CANDIDA SP.</u>		SEAWATER + PY	4+	±	-	±
<u>PSEUDOMONAS</u> M.		SEAWATER	+	+	±	+
<u>FUSARIUM</u> SP.		SEAWATER + PY	3+	4+	3+	4+
<u>CLADOSPORIUM</u> R. #6	CREOSOTED PILING	FRESH WATER	3+	±	2+	

* - : NO SURVIVAL

± : SURVIVAL BUT QUESTIONABLE GROWTH

+ TO 4+: INCREASING DEGREES OF GROWTH

BASIC RESEARCH NEEDS

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Following the Fuels Workshop on June 15-16, the Chairman examined the written summaries and digested the closing discussion. The results of this process are presented in the following paragraphs.

Many research and technology needs surfaced at the Workshop. On most subjects, it is obvious that we must undertake basic research and applied research programs before synthetic fuels can be used in U.S. Navy aircraft. Although efforts throughout the range of R&D were presented, the following outline will focus on basic research needs, the major aim of the Workshop.

Stability - Jet fuel stability has been of concern for 25 years, throughout most of the jet age. Stability will become even more important as we start to use synthetic jet fuels because of the greater content of compounds containing hetero atoms. Thermal oxidative stability has been a greater problem than storage stability. In spite of many studies, our knowledge of fuel oxidation and stability is primarily empirical. In view of the key role of this fuel property, basic research must be addressed in anticipation of the utilization of synfuels. Specific basic research areas which should prove fruitful are:

- Define the role of hetero atom compounds in fuel stability
- Study the mechanism of homogeneous and heterogeneous catalysts in thermal oxidative stability
- Delineate the chemistry of peroxidation of hydro-treated fuels

Low Temperature Properties - Relief on the availability of jet fuel could come by raising the distillation end point. A higher freezing point and viscosity will probably accompany this change. The freezing point, in particular, will be a problem area for shale derived fuels. Some aircraft mission adjustments or hardware modifications may permit some relaxation on freezing point and viscosity. Basic research on composition/property relationships will be useful, however as synfuels are introduced.

- Isolate and identify compounds which precipitate from fuel near its freezing point
- Define non-ideal freezing point behavior of multi-component hydrocarbon mixtures and fuels
- Develop a viscosity model for multi-component mixtures of hydrocarbons

Combustion - Jet engines will face combustion problems with synfuels since these fuels will have higher aromatic contents and lower hydrogen contents. If this fuel composition is combined with a higher distillation end point, significant difficulties can be envisioned. Much of the effort in this field will be applied research, but some basic research topics can be identified.

- Atomization and vaporization studies on higher viscosity fuels
- Mechanism of soot formation
- The role of H/C ratio with varying hydrocarbon structure
- NO_x control and mechanism studies
- Mechanism of soot reduction with water addition
- Combustion enhancement by microwaves and electric fields

Catalysis - Catalysts are important in producing fuels from alternate sources such as oil shale, coal and tar sands. Catalysts may also be useful in solving combustion difficulties. On the other hand, hot metals can catalyze the formation of degradation products in the aircraft fuel system. Suggested areas of research in catalysis are itemized below.

- Develop improved cracking and hydrocracking catalysts which are immune to nitrogen and sulfur poisoning
- Develop catalysts for isomerizing the high concentrations of n-alkanes in shale jet fuels

- Combustion enhancing catalysts
- Fuel reforming processes
- Mechanism of jet fuel degradation on hot metals or with dissolved metal salts and complexes
- Fuel ignition on hot surfaces

Jet Fuel Additives - Although additives have been useful in modifying undesirable fuel properties, they frequently effect secondary problems. Thus, fuel additives must be used only after extensive testing. Nevertheless, additives must be considered for property improvement in view of the shortage and cost of petroleum fuels and the prospect of using synfuels. Fruitful areas for additive research are shown below.

- Flow improvers for waxes in jet fuels
- Dispersants for solid degradation products that do not inhibit water removal
- Non-metallic smoke suppressants
- Mechanisms of smoke suppression
- Additive interactions
- Development of multifunctional additives

Handling Problems - The toxicity of petroleum jet fuels has received little study in the past but current research is looking for environmental problems with these materials. These studies must be extended to synfuels made from shale, coal and tar sands. The microbiological behavior of petroleum jet fuels is well known but synfuels need to be studied in the future.

Analysis - In developing information on synthetic jet fuels we need to go beyond mere specification tests. We should define these new materials in considerable detail prior to introduction into the fleet. This will put us in a position to develop composition/property relationships, to anticipate problems, and to be able to respond rapidly to difficulties as aircraft begin

to burn synthetic jet fuels. The following composition information is needed.

- Types and amounts of hetero atom compounds (fuel stability, combustion, and toxicity)
- Types and amounts of aromatic hydrocarbons (combustion, toxicity, peroxidation, and fuel stability)
- Amounts of n-alkanes and other symmetrical molecules (freezing point)
- Types and amounts of polycyclic hydrocarbons (combustion and peroxidation)

WORKSHOP SUMMARY

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This workshop has focused on the fuels for future use in aircraft. We need to remember, however, that other parts of the Navy are involved in obtaining, delivering, and storing fuel for Navy aircraft. Certainly the aircraft carrier is a vital element in the fuel chain from refinery to aircraft. Thus communication between aircraft, ship, and even headquarters personnel is important in arriving at meaningful specifications and properties for jet fuels. It is likewise necessary to communicate between various people in the R&D chain - from those doing basic research to those designing fuel systems and engines.

The Navy must be ready to fight, not only in an abnormal situation such as Viet Nam, but also when the enemy is sending missiles and other ordnance at Navy vehicles. Thus we require a fuel we can depend on, one that meets the needs of the jet engine. What chance does the aircraft have in action if any of its systems are inoperative or in marginal condition? Since many of the aircraft in the current inventory will be in service for twenty years or more, the Navy jet fuel for the next two or three decades must look pretty much like today's JP-5.

One fuel aspect not highlighted in the workshop is that of safety. The Navy is very conscious of the fire potential of hydrocarbon fuels. Therefore, we require a relatively high flash point of 140°F for JP-5. This requirement is primarily a protective feature for the aircraft carrier where huge quantities must be stored. The value of a high flash point has been proven in situations such as a fire on the USS MIDWAY. Under other circumstances, such as the KENNEDY-BELKNAP collision, even a JP-5 fire can be difficult to control.

We have observed from analysis of petroleum crudes and of submarine atmospheres contaminated with petroleum solvents that petroleum is a fairly consistent material regardless of the specific source. Is this consistent composition characteristic of shale oil and coal liquids? Is the composition of shale fuels similar to that of petroleum fuels? Do we need new tests or analysis to define synfuels? We don't know the answers to these questions. We do know, however, that current

specifications were developed for petroleum derived fuels. Hence, we expect that changes in specification requirements and tests will be needed as we gain more knowledge about shale and coal synfuels.

With regard to specific research areas, we make the following comments. Refining of synfuels can make suitable fuels. However, we will have to put the right items in the specifications and depend on the refiner to make a satisfactory product. In this effort, we will have to learn how to use our refining capabilities in the most efficient and integrated combinations.

Fuel stability will be marginal for synthetic jet fuels because of the hetero atom content of the source material. Long term storage stability and high temperature oxidative stability will require empirical solutions in the next few years, but greater chemical understanding of fuel instability should be forthcoming in the next decade.

It appears that only the early stages of combustion are dependent upon hydrocarbon structure. Thus if we can learn to force combustion through the early stages, the burning of hydrogen and carbon monoxide in the late stages can occur smoothly. The important control on combustion behavior - smoke production and flame radiation - then could be the H/C ratio.

We may have to compromise our requirements on low temperature properties. The aircraft may have to be modified to limit the temperature to which the fuel is exposed. In this regard, the exposure conditions and mission profiles need to be re-examined.

Additives offer hope of alleviating some property limitations exhibited by synthetic jet fuels. Caution must be exercised, however, since an additive frequently creates a problem while simultaneously improving another problem. Our knowledge of interactions between additives is definitely inadequate.

This is the time to pursue detailed fuel analysis. We must go beyond the specification tests developed for petroleum derived fuel and be alert for composition differences which influence properties.

The physiology, toxicity, and bacteriology of synfuels are wide open subjects. The efforts which are just beginning will give the Navy important guidance in how to store, transport, and handle these new fuels.